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THE PHOTODEGRADATION OF POLYACRYLONITRILE
IN SOLUTION

A Thesis
Presented to
the Faculty of the Graduate School
Assumption University of Windsor

In Partial Fulfillment
of the Requirements for the Degree
Master of Science in Chemistry

by
Ivan Jack Bastien
May 1961

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ABSTRACT

Polycrylonitrile was degraded in a solvent mixture of ethylene carbonate and propylene carbonate, (80:20 by weight) by exposing solutions of the polymer to ultraviolet radiation of wavelength 253.7 mμ. The degradation was studied as a function of concentration of polycrylonitrile in the solvent mixture, original number average chain length, and the incident light intensity. The course of the degradation was followed by intrinsic viscosity measurements.

The decrease in intrinsic viscosity was used as a measure of chain scission occurring in the photodegraded polymer. The results were represented by the generalized random chain scission theory for photodegraded polymers in solution.

The study of the chain scission process was complicated by the general increase in optical density of the photodegraded polymer solutions. Also, the choice of the proper intrinsic viscosity-number average molecular weight relationship for the kinetic representations was not certain. A search of the literature indicated that the Claxand and Stockmayer equation was the best.

The experimental results indicated that the degradation was independent of the concentration of the polymer and bore a direct relationship to the first power of the incident light intensity. The degradation, when

measured in terms of the intrinsic viscosity, appeared to be independent of the original intrinsic viscosity for different polymer samples.

Two samples obeyed the random chain scission theory well, in that the rate constants for the two samples were approximately the same. A sample of different history followed the random chain scission theory but its rate constant was different.

The experimental results also indicated the presence of new chemical groups in the degraded polymer system. These groups were characterized by the appearance of two peaks at 216 and 295 m μ , in the ultraviolet absorption spectra of the degraded polymer solutions.

The polymer solutions also increased in absorption at 2536 A^o during the degradation. Quantum yield determinations were calculated on the basis of an average optical density for the exposed polymer solutions. A quantum yield of 0.8×10^{-4} chain scissions per quantum absorbed is reported.

ACKNOWLEDGEMENTS

The author wishes to express his appreciation to Dr. E. H. G. Jellinek for the interest and guidance he so willingly gave in the course of this investigation.

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CHAPTER I

THE PROBLEM AND DEFINITIONS OF TERMS USED

I. THE PROBLEM

Very little work has been done on the photodegradation of polyacrylonitrile in solution. As a matter of fact, investigations of the photodegradation of polymers are not very numerous in contrast to work on degradation by high energy radiation such as x-rays, γ -rays, electrons and neutrons.

The degradation processes initiated by ultraviolet radiation are quite complex and the elucidation of the kinetics and the mechanisms of the reactions is difficult.

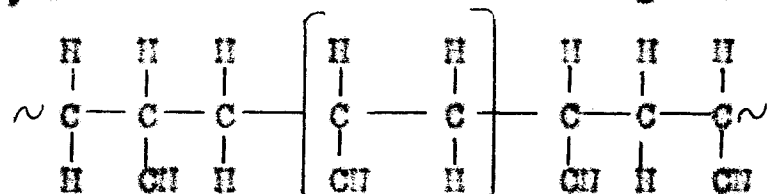
An investigation of the breakdown of polyacrylonitrile molecules in solution by the action of ultraviolet light was carried out by Jellinek and Schlueter (1) who showed that the degradation was approximately obeyed by a random scission process. However, problems concerning the photodegradation of polyacrylonitrile remained to be solved. The present work is a continuation of the study of the degradation of polyacrylonitrile; some experiments were repeated with a greater degree of accuracy than was possible in the previous work and the investigation has been extended to

the photodegradation as a function of polymer concentration and polymer chain length. Further ultraviolet absorption spectra and infrared absorption spectra of polyacrylonitrile at various stages of the irradiation process have been studied in detail. Preliminary experiments have also been carried out with polyacrylonitrile films and model substances of small molecular weight related to polyacrylonitrile. In the discussion of the experimental results, data obtained by other workers on the thermal degradation of polyacrylonitrile have also been considered. On the basis of all these experimental data, likely mechanisms for the photodegradation process are considered. The photodegradation of polyacrylonitrile was studied in solution rather than in its bulk state in the form of a film or a powder for the following reason: When a polymer film is irradiated with ultraviolet light usually chain scission and crosslinking of polymer chains take place simultaneously. However, it is to be expected that in dilute polymer solutions the crosslinking reaction would be largely suppressed and consequently the chain scission reaction could be studied on its own. This would simplify the elucidation of the mechanism. As a matter of fact, the experimental data show, that indeed in solution predominantly a chain scission reaction takes place. In addition to the scission process, reactions of the side groups of the polymer chains also occur.

The Random Chain Scission Process

"A multitude of degradation mechanisms could in principle be worked out; however, it is better to confine oneself to mechanisms which have been shown by experiment to be realized, or at least not to be unlikely. One of these modes of breakdown of long chain molecules is described by the theory of random breaking of links (2)." The object is to find expressions for the average molecular weights and chain lengths, and the average number of broken links for one original chain as a function of time.

The polymer polyacrylonitrile is an addition polymer, and is considered to be a straight chain molecule,



It is apparent that the polymer is comprised of repeating units, one of which is shown bracketed. The chain length "P" is the number of units in the chain. Knowing the molecular weight of the polymer chain, one can easily determine its chain length. If M_1 represents the molecular weight of the monomer or one mer unit, the chain length is given by

$$P = M_p / M_1 \quad (1)$$

where M_p is the molecular weight of the polymer molecule of chain length P.

Since usually a polymer sample is not homogeneous, that is, it does not have chains of one length only, average values are used for expressing molecular weights of polymers and their chain lengths.

For a polymer, whose main links in the chain are ruptured at random, an equation can be derived which relates the so-called number average chain length P_t with the corresponding time t of the degradation process:

$$1/P_t - 1/P_0 = kt \quad (2)$$

where P_t is the number average chain length at time " t ". P_0 is the number average chain length at the beginning of the degradation process ($t = 0$) and k a rate constant.

Equation (2), however, is not a sufficient criterion for showing that a random chain scission process is operative. It has also to be demonstrated that a rapid decrease of chain length with time takes place and that the amount of monomer produced during degradation is negligible.

II. DEFINITION OF TERMS USED

There are numerous terms used in this thesis which require definition and explanation. Some terms have already been defined. However, in order to give a summary of specific terms, Table I was prepared. The symbols are primarily those found in the monograph on the 'DEGRADATION OF VINYL POLYMERS' by H. H. G. Jellinek (2).

TABLE I

M_1	Molecular weight of monomer
M_p	Molecular weight of chains of length P
M_n	Number average molecular weight
M_v	Viscosity average molecular weight
M_w	Weight average molecular weight
P	Chain length
P_n	Number average chain length
P_0	Initial or original chain length
P_t	Number average chain length at time " t " of the degradation process
η_r	Relative viscosity
η_{sp}	Specific viscosity
$[\eta]$	Intrinsic viscosity
η_0	Viscosity of solvent
η_c	Viscosity of solution of concentration c
n_p	Number of molecules of chain length P
a	Exponential constant in molecular weight-viscosity relationship
n_0	Number of links at start of degradation
n_t	Number of links at time " t "
α	Degree of Degradation
k	Rate constant
I_0	Incident light intensity

TABLE I (Continued)

I.....	Light intensity (generally)
ϕ	Quantum yield
E.....	Extinction coefficient
DMF.....	N-N dimethylformamide
PAN.....	Polyacrylonitrile
S.....	Average number of breaks for each original chain

CHAPTER II

LITERATURE REVIEW

Which has been written on the degradation of polyacrylonitrile by chemical means pyrolysis, and high energy radiation, (1, 3, 4, 5, 6, 7, 8, 9, 10, 11), as already mentioned above. Some preliminary work has been done on the photodegradation of PAN (polyacrylonitrile) as a function of the incident intensity of the light source. A brief summary of the degradation reactions as well as those of other polymers will be given here.

I. LITERATURE ON THE DEGRADATION OF POLYACRYLONITRILE

Polyacrylonitrile has been studied by various authors. The main results are summarized in Table II.

TABLE II

DEGRADATIONS OF POLYACRYLONITRILE

<u>Author</u>	<u>Type of Degradation</u>	<u>Products</u>
Houtz (4)	thermal (bulk)	2-amino pyridine structures in polymer
Burlant and Parsons (5)	thermal (bulk)	internally cyclized naphthyridine rings in the polymer structure
Burlant and Taylor (6)	1 mev electrons (films)	N ₂ atmosphere crosslinked O ₂ atmosphere chain scission
Straus and Madorsky (3)	thermal (bulk)	volatile products mainly HCN acrylonitrile vinyl acetonitrile
McCartney (7)	alkaline degradation in DIF	keteno-imine structures or internal cyclization
Kobayashi (8)	thermal (bulk)	internally cyclized pyridine rings
Sokolova, Kudryavtsev, and Strepikheev (9)	hydration in DIF	internally cyclized piperidine rings
Jallinek and Schluter (1)	photodegradation in solution	no change in structure random chain scission
Schurz (10) (11)	thermal (bulk)	crosslinked by iminization

It will be noticed that there is little agreement as to the nature of the cyclized product in the thermally degraded polymer. The only quantitative measurements of volatile products were carried out by Strans and Madorsky (3). Some of their typical results are given below.

TABLE III

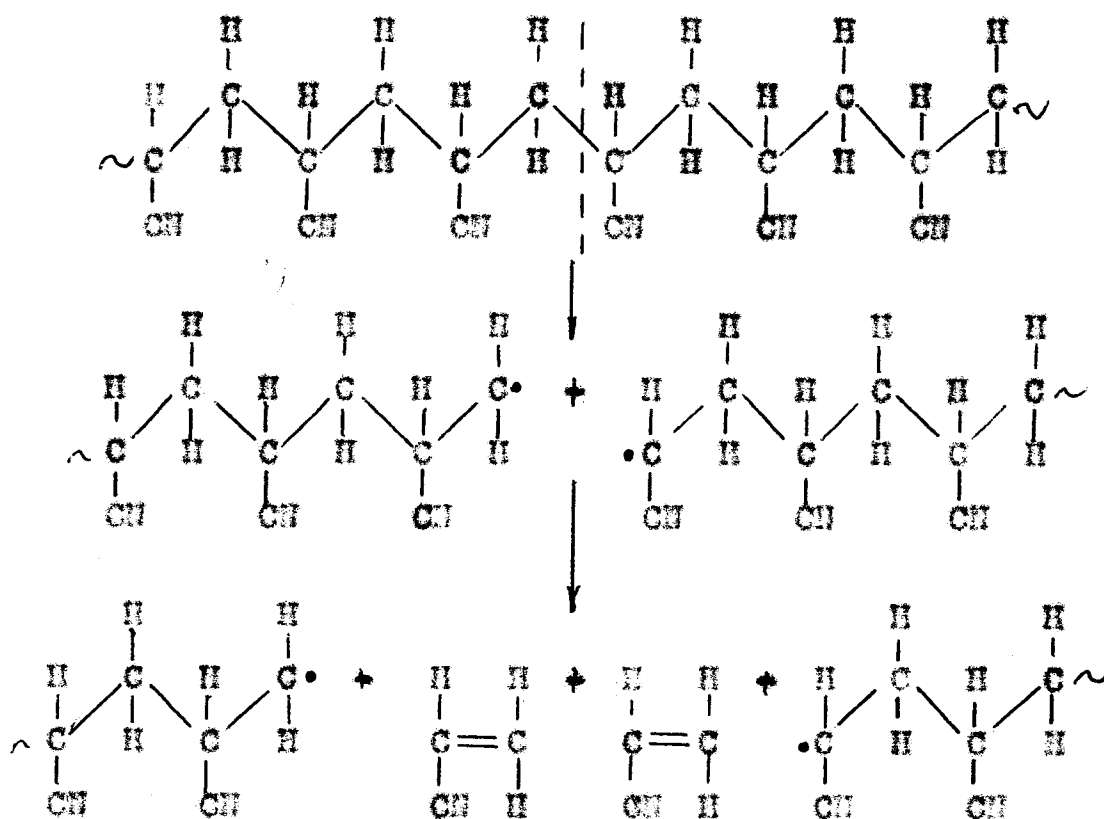
MASS-SPECTROMETER ANALYSIS OF VOLATILE FRACTIONS FROM
PYROLYSIS OF POLYACRYLONITRILE AT 275° C.

Component	Time Interval Between End Of Experiment and Analysis		
	1 to 2 Hours	1 Day	1 Week
	Mole %	Mole %	Mole %
Hydrogen Cyanide	34	—	—
Acrylonitrile	36	88	86
Vinylacetonitrile	30	12	14
Pyrrole	—	—	—
Acetonitrile	—	—	—
Butyronitrile	—	—	—
Propionitrile	—	—	—

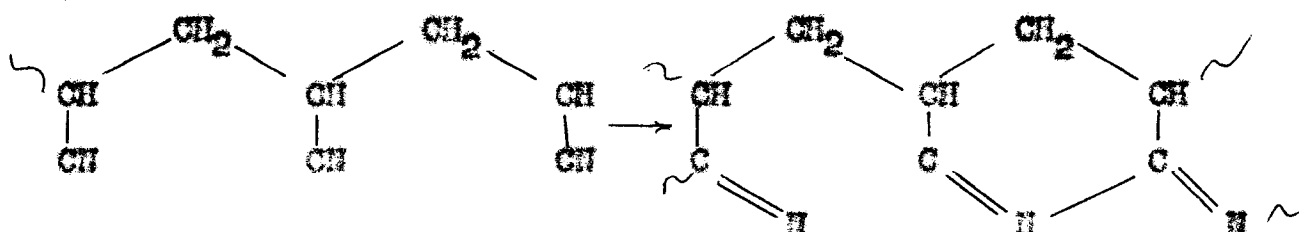
The fractions volatile at 25°C. but not at -190°C. were collected. The main constituents of the fractions were HCN, acrylonitrile, and vinylacetonitrile. The composition of the fraction depended on the time interval

olapsing between pyrolysis and analysis. Straus and Madorsky (3) suggested that some of the components, particularly HCN and acrylonitrile, react and become non-volatile on standing and, as a result, the remaining volatile constituents become accentuated in the analysis. Whereas Durlant and Parsons (5) indicated that ammonia was a degradation product, Straus and Madorsky found no ammonia in the volatiles.

Straus and Madorsky visualized the formation of monomer as follows. "A random scission of a C-C bond in the chain results in two free radical ends," and an unripping reaction yielding monomer.

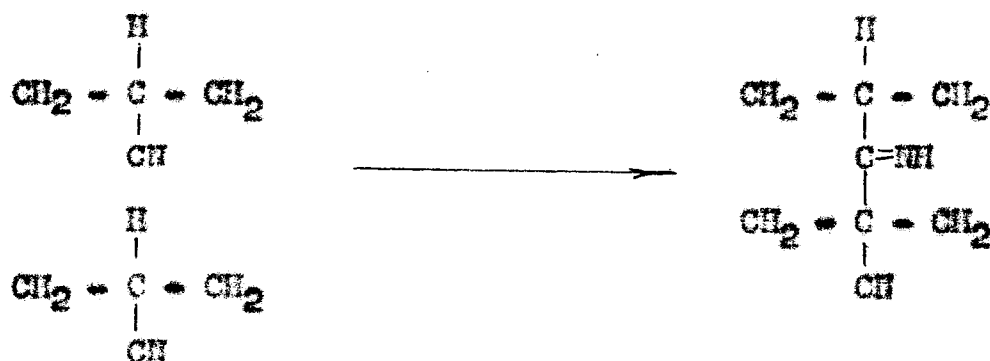


The fact, that most authors have indicated that internal cyclization takes place during the degradation of PAN within the polymer structure, seems to suggest that the degradation does not only consist of a random chain scission process. Burlant and Parsons (5) have offered evidence for aromatization within the polymer structure,



Their conclusions were based on the analysis of reaction products by infrared spectrophotometry.

In all cases of degradation, the polymer eventually turned from yellow through orange to brown. Different mechanisms have been advanced to account for this discolouration. Schurz (10, 11) pointed out that this is due to the crosslinking of the polymer. He based his conclusions on the marked decrease in solubility and increased ultraviolet absorption of the polymer. The crosslinking reaction is pictured by this author as follows:



Intramolecular cyclization may also be considered as an explanation for the discolouration of the polymer (see Table II).

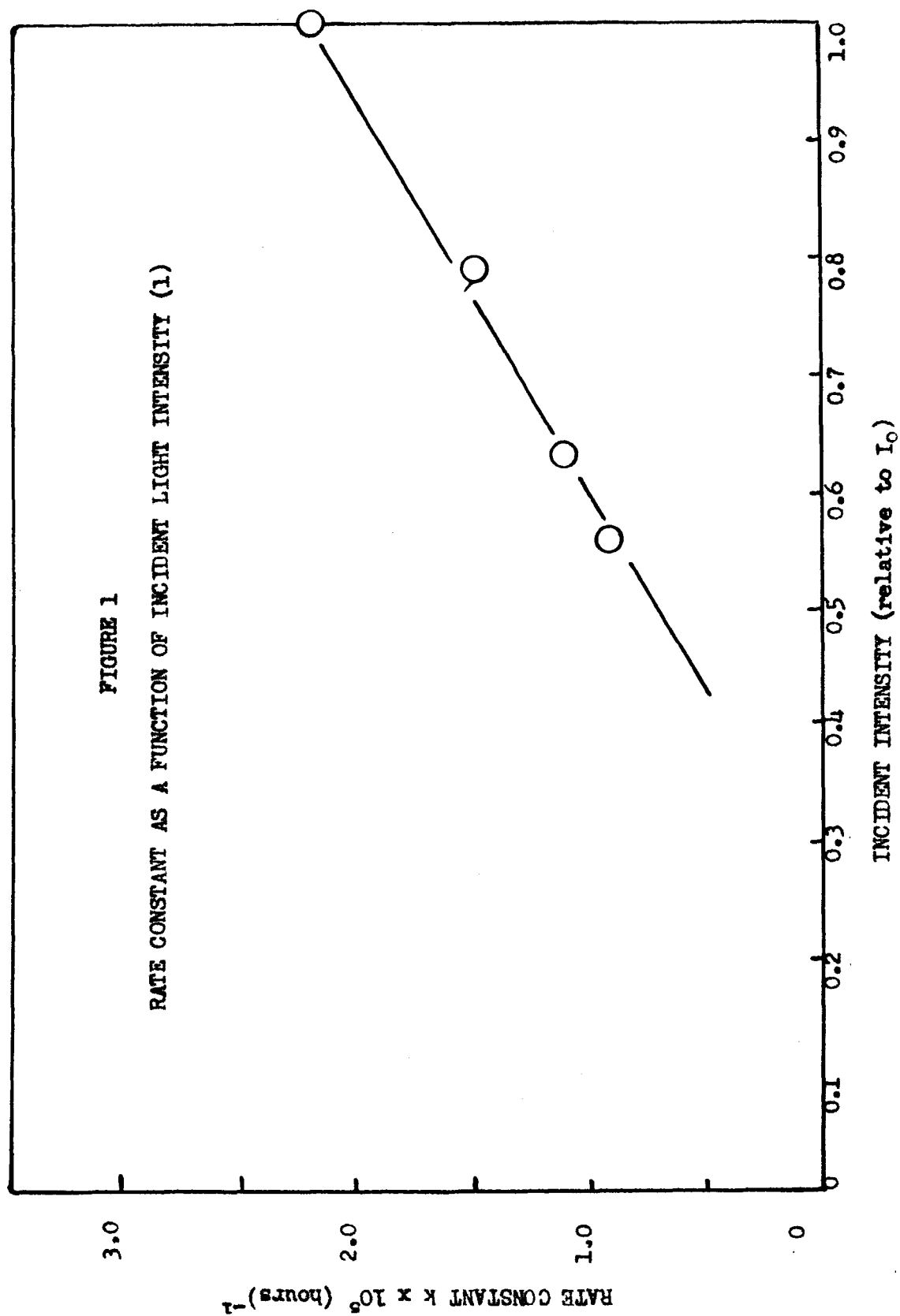
Although the information discussed above has been obtained from degradation reactions other than photodegradation, similarities in chemical change for photodegradation and other types of degradation are quite possible.

The most intensive work on the photodegradation of polyacrylonitrile was done by Jellinek and Schlueter (1). They indicated that there was no change in structure of the polymer. Their work was primarily concerned with the determination of the rate of degradation and its dependence on the radiant intensity. Their results for the rate constants of photodegradation as a function of light intensity could be represented by a straight line relationship, however, this line did not pass through the origin of the coordinate system as is shown in Figure 1. This behaviour necessitated a re-examination of Jellinek and Schlueter's experimental data (1).

Re-analysis of the Photodegradation of Polyacrylonitrile

The results of the work by Jellinek and Schlueter (1) may be summarized as follows:

The ultraviolet photodegradation of polyacrylonitrile in a mixture of ethylene carbonate and propylene carbonate (80 : 20% by weight) was studied by exposing solutions of



0.2% w/v of PAN in the solvent mixture to light of wave length 2537 Å. Preliminary results showed that in the presence of oxygen, chain scission takes place, but in its absence, some chain scission and recombination of radicals seemed to occur. Quantitative studies on polymer solutions under vacuum were performed by determining intrinsic viscosities as a function of exposure time, and as a function of the light intensity. Plots of $1/P_t$ vs. t were approximately linear, but the individual experiments show rather a large scatter. It was also found that in the range investigated, the rate constants decreased linearly with decreasing light intensity and as already pointed out, approached zero at some finite intensity. The behaviour was not accounted for. The quantum yield was found to be 7.7×10^{-4} chain ruptures for each quantum absorbed. Infrared spectra indicated that there was no pronounced change in the overall structure of the polymer. It was also observed that the ultraviolet light absorption of the polymer in solution increased (13).

A careful analysis of the intensity-rate constant relationship is necessary and is outlined on page 16. As the rate is proportional to the light intensity, or to be more exact, the intensity raised to some power "n", the ratio of the rate constant at two different light intensities should have been equal to the ratio of their light intensities raised to the power "n", i.e.

$$k_1/k_2 = (I_1/I_2)^n \quad (3)$$

A much better estimate of "n" could be obtained by plotting the rate constants "k" vs I^n which should be a linear relationship. Such a plot was made for Jellinek and Schlueter's experimental data (1) where "n" was found to be 1.5. (See Figure 2)

An exponent $n = 1.5$ cannot be reconciled with an ordinary random scission process. Before accepting such an exponent it was clearly desirable to investigate other possible causes for this strange rate constant-light intensity relationship. For the evaluation of the experimental data an intrinsic viscosity-number average molecular weight relationship was employed by Jellinek and Schlueter (1) which was experimentally derived by Onyon (18). However, a search of the literature revealed that there is quite a large number of intrinsic viscosity-number average molecular weight relationships presented by various authors. The relationship has the general form

$$[\eta] = K \bar{M}_n^a \quad (4)$$

where K and "a" are constants. Parameters given by various authors are contained in Table IV. More recently the relationship by Cleland and Stockmayer is believed to be the best one. A re-analysis of all the data obtained by Jellinek and Schlueter (1) using the Cleland and Stockmayer equation (17) has been carried out and is discussed below.

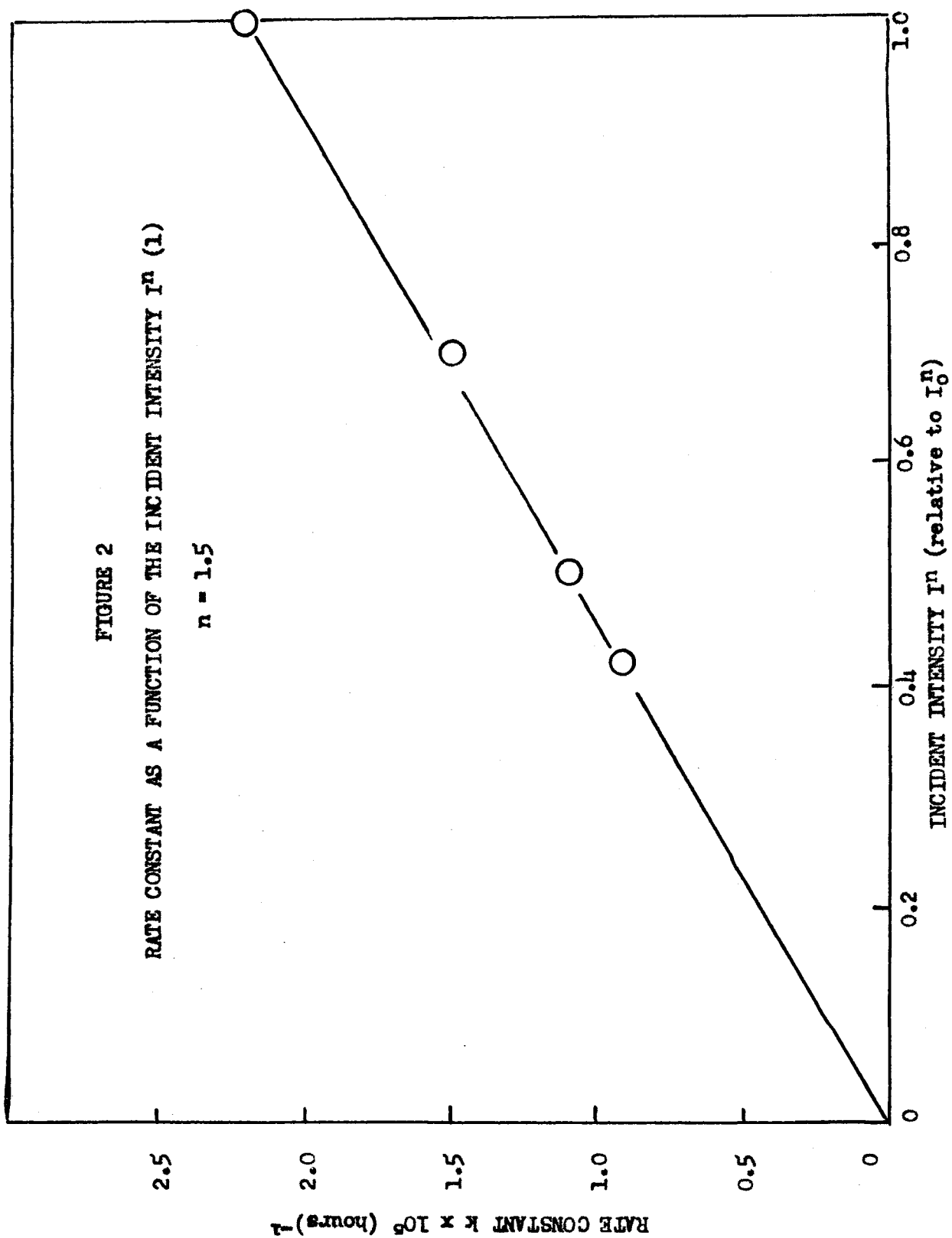


TABLE IV

NUMBER AVERAGE MOLECULAR WEIGHT-INTRINSIC VISCOSITY

RELATIONSHIP

FOR PAN IN N-N DIMETHYL FORMAMIDE AT 25°C

Author	Details	M_n Range $\times 10^{-3}$	$10^3 \eta$	a
Houtz (4)	O, F	18-135	1.75	0.66
Frind (14)	O, P, A	9-69	2.50	0.66
Ciampa (15)	O, F, A	12-61	0.04	1.0
Disschops (16)	S, F	46-270	0.166	0.81
Cleland and Stockmayer (17)	L, P, S	15-132	0.233 ^a 0.243 ^b 0.392 ^c	0.75 0.75 0.75
Onyon (18)	O, P, B	177-1000	1.97	0.625
(19)	Unfractionated (Transfer and Disproportion- ation)	28-1000	0.392	0.75
(19)	Unfractionated (Combination)	28-1000	0.320	0.75
Danzford et al (20)	Transfer	2.5-25	0.574	0.733
(20)	Combination	2.5-25	0.472	0.733
Krigbaum and Kotliar (21)	O, S, L, F	33-101	.155	0.80

Abbreviations: O, osmometry; S, sedimentation velocity;
L, light scattering; S, solution polymerization in various
solvents; P, fractionated polymer; A, aqueous solution
polymerization; B, bulk polymerization; a, weight average

Abbreviations (Continued): molecular weight; b, viscosity average molecular weight; c, number-average molecular weight assuming $M_v = 2M_n$

Re-Evaluation of the Kinetics of Degradation

All number average chain lengths at various stages of the degradation process were determined by Jellinek and Schluster (1) using the equation,

$$[\eta]_{\text{EPC}} = 8.9 \times 10^{-3} M_n^{0.47} \quad (5)$$

where $[\eta]_{\text{EPC}}$ is the intrinsic viscosity

in $(\text{ga}/100 \text{ ml})^{-1}$ in a solvent mixture of ethylene carbonate and propylene carbonate (80:20 by weight).

Equation 5 was obtained as follows. The intrinsic viscosities of three polymer samples in dimethylformamide were determined. By use of the equation given by Onyon (18)

$$[\eta]_{\text{DMF}} = 1.97 \times 10^{-3} M_n^{0.625} \quad (6)$$

the number average molecular weights were obtained. Further the intrinsic viscosities of the samples were determined in the ethylene carbonate-propylene carbonate solvent mixture. Knowing the number average molecular weights, the parameters "K" and "a" could be evaluated, yielding equation (5).

The process was repeated in this work using the Cleland-Stockmayer equation (17) for dimethylformamide,

$$[\eta]_{\text{DMF}} = 0.392 \times 10^{-3} M_n^{0.75} \quad (7)$$

From these measurements and measurements in the solvent mixture, the parameters for the intrinsic viscosity-number average molecular weight relationship in the solvent mixture could be derived. The results are summarized in Table V.

TABLE V

NUMBER AVERAGE MOLECULAR WEIGHTS AND INTRINSIC VISCOSITIES

$[\eta]_{\text{DMF}} \text{ (g/100 ml)}^{-1}$	$[\eta]_{\text{EPC}} \text{ (g/100 ml)}^{-1}$	M_n
2.19	1.65	99,100
1.40	1.21	54,590
0.81	0.78	26,320

DMF Intrinsic Viscosity in N-N dimethylformamide

EPC Intrinsic Viscosity in solvent mixture

The average value for "a" is $0.56 \pm .04$

The average value for "K" is $2.65 \times 10^{-3} \pm .03 \times 10^{-3}$

Hence the new equation for the determination of M_n values using the solvent mixture is

$$[\eta]_{\text{EPC}} = 2.65 \times 10^{-3} M_n^{0.56} \quad (8)$$

From the data available, it was possible to determine the number average chain lengths as a function of exposure time. The results of these calculations are comprised in Table VI. By plotting $1/P_t$ against time of

irradiation for previous incident light intensities, straight lines are obtained from which the rate constants were calculated. The straight lines were obtained from the data which best fitted the theory for the random scission process. (See Figure 3)

By using the new intrinsic viscosity-number average molecular weight relationship, all number average chain lengths are appreciably different from those derived by Jellinek and Schluster (1). As a consequence, the rate constants have also different numerical values. The new rate constants and the corresponding incident light intensities are shown in Table VI.

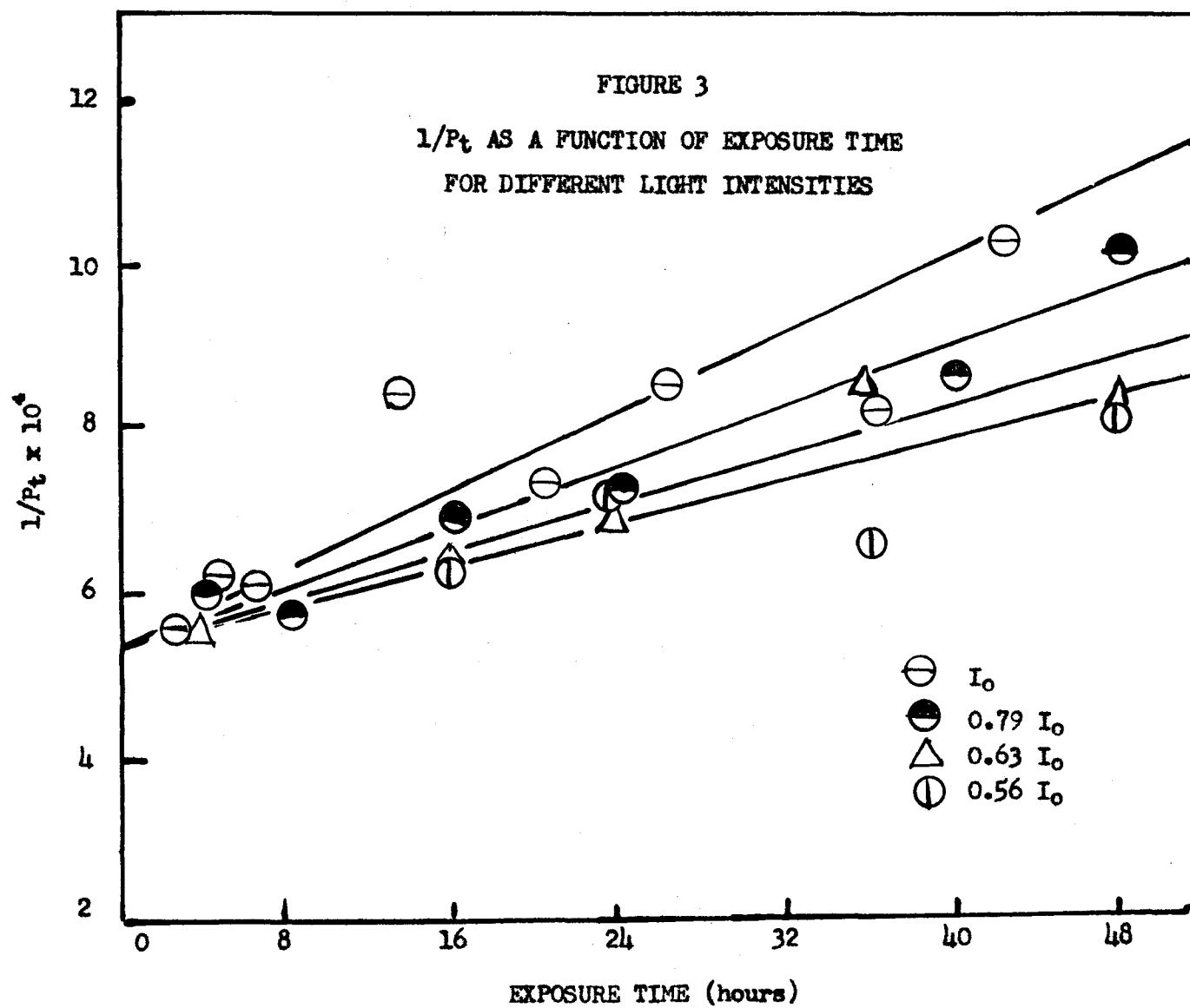


TABLE VI

$1/P_t$ AS A FUNCTION OF TIME OF EXPOSURE FOR FOUR INCIDENT
LIGHT INTENSITIES (CONCENTRATION 0.2% W/V)

(DATA FROM JELLINEK AND SCHLUETER (1) WITH RECALCULATED P_t VALUES)

<u>t Hours</u>	<u>$[\eta]$ (gm/100 ml)⁻¹</u>	<u>P_t</u>	<u>$1/P_t$</u>
0	1.65	1.87×10^3	5.30×10^{-4}
2	1.61	1.76	5.68
4	1.53	1.61	6.23
8	1.55	1.64	6.08
13	1.30	1.20	8.33
20	1.40	1.37	7.29
24	1.29	1.18	8.44
36	1.32	1.23	8.11
42	1.16	0.981	10.19
48	0.98	0.725	13.8

<u>t Hours</u>	<u>$[\eta]$</u>	<u>P_t</u>	<u>$1/P_t$</u>
0	1.65	1.87×10^3	5.30×10^{-4}
4	1.55	1.64	6.08
8	1.59	1.72	5.81
16	1.44	1.44	6.93
24	1.40	1.37	7.29
40	1.28	1.17	8.56
48	1.17	0.996	10.04

$0.79I_0$

TABLE VI (Cont'd)

<u>0.63 I₀</u>			
<u>t Hours</u>	<u>[η]</u>	<u>P_t</u>	<u>1/P_t</u>
0	1.65	1.87x10 ³	5.30x10 ⁻⁴
4	1.61	1.76	5.68
16	1.49	1.53	6.52
24	1.43	1.42	7.02
36	1.28	1.17	6.56
48	1.30	1.20	8.33

<u>0.56 I₀</u>			
<u>t Hours</u>	<u>[η]</u>	<u>P_t</u>	<u>1/P_t</u>
0	1.65	1.87x10 ³	5.30x10 ⁻⁴
16	1.50	1.55	6.45
24	1.40	1.37	7.29
29	1.49	1.53	6.52
48	1.31	1.22	8.21

The rate constant "k" is plotted for each intensity in Figure 3 and tabulated below.

TABLE VII

RATE CONSTANTS AS A FUNCTION OF LIGHT INTENSITY

<u>Relative Intensity</u>	<u>k Hours⁻¹</u>
I_0	1.17×10^{-5}
$0.79I_0$	0.90
$0.63I_0$	0.72
$0.56I_0$	0.62

Figure 4 shows a linear relationship between intensity and the rate constant at a constant concentration.

It is apparent that the rate of degradation is now proportional to I . Moreover, the rate constant is zero at zero intensity, while the rate constant using the Onyon equation has a finite value at zero light intensity.

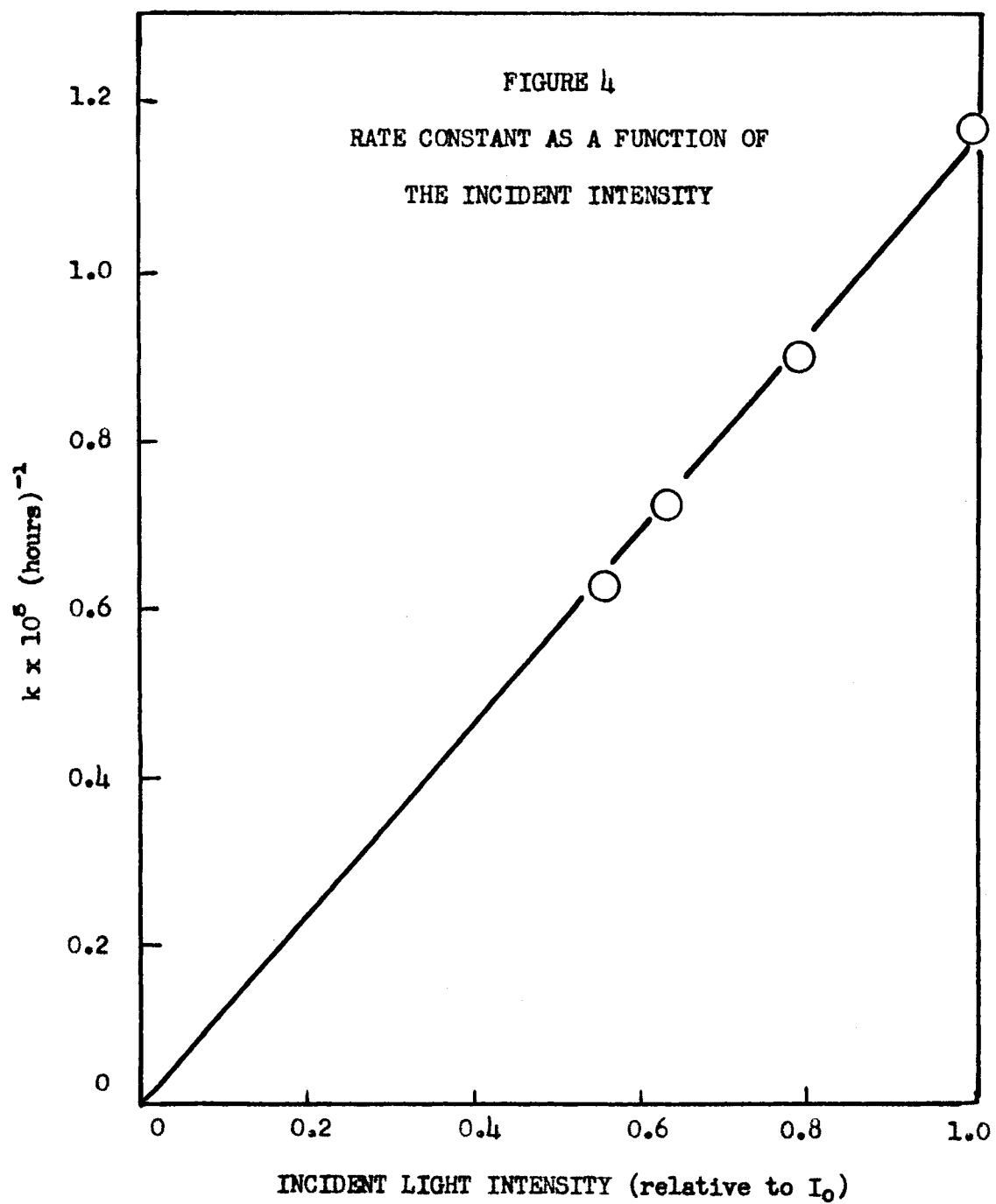
The results obtained by the use of the Cleland-Stockmayer equation seem to indicate that it is the best intrinsic viscosity-number average molecular weight relationship to adopt for the present work.

Photodegradation of Other Polymers

Other polymers also degrade by the random chain scission process when they are exposed to ultraviolet

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radiation, except for polymethylmethacrylate. The results obtained by various authors are summarized in Table VIII.

TABLE VIII

QUANTUM YIELDS ϕ IN BONDS BROKEN FOR EACH
QUANTUM ABSORBED FOR VARIOUS POLYMERS

Polymer	Variable Measured	Wave-Length \AA°	ϕ	Reference
Polyethylene-terephthalate	H_n	2800-3600	5.0×10^{-4}	Osborn(22)
Rubber	Gas evolved	2500-4000	4.0×10^{-4}	Datenan(23)
Cellulose (paper)	P_n	2537	10^{-3}	Leamer and Wilson(24)
Cellulose acetate	H_n	2537 3600	$\frac{1}{10^{-4}}$	Sippel(25)
Polymethyl-methacrylate	Monomer evolved	2537	220	Crowley & Melville(26)
Polymethyl-methacrylate	Gas evolved	3030-3130	0.23×10^{-3}	Frolova & Ryabov (27)
Benzoguanamine resin	Thiazine & phenyl rings	----	4.0×10^{-4}	Gusman & Spell(28)
Polyethylene	Formation of carbonyl	2537 2500-3500	4×10^{-2} 1×10^{-1}	Burgess(29)
Polystyrene	H_v	2537	1.7×10^{-5}	Shih-Wei Chen(30)
Polyacrylonitrile	H_n	2537	7.7×10^{-4}	Jellinek & Schluster(1)
Cellulose acetate	P_n	254-434	2.5×10^{-3}	Jortner(31)
Poly- α -methylstyrene	Monomer formed	3030-3130	7×10^{-3} @ 27°C 0.5 @ 115°C	Stokes & Fox (32)
Poly- α -methylstyrene	H_v	----	1.1×10^{-3} @ 27°C 2×10^{-3} @ 115°C	Stokes & Fox (32)

It is interesting to compare the quantum yields obtained for the photodegradation of the polymers. Except for the quantum yield for polymethylmethacrylate (26), which is known to be a reverse polymerisation process with chain end initiation, all quantum yields are very small and of a similar order of magnitude agreeing with the assumption of a random chain scission process.

Now experiments on the photodegradation of polyacrylonitrile in solution are discussed in the following chapter.

CHAPTER III

EXPERIMENTAL METHOD

General Method

Polyacrylonitrile samples were dissolved in an 80:20 mixture by weight of ethylene carbonate and 1,2 propane diol cyclic carbonate. The solutions, which were under vacuum, were exposed to an ultraviolet lamp emitting energy of wave length 2537 angstroms. After exposure of the samples, intrinsic viscosities and ultraviolet absorption spectra were determined. Other measurements consisted of determining change in infrared spectra of exposed samples in different states; i.e. solution, powder, and film. Quantum yield measurements were determined using the uranyl oxalate-oxalic acid actinometer system (31, 32).

Preparation of Materials

(1) Materials - methanol (acetone free); Baker and Adams. N-N dimethylformamide (spectrograde); Eastman-Organic Chemicals.

- Polyacrylonitrile samples were supplied by the Chemstrand Corporation.

- Ethylene Carbonate and 1,2 propanediol cyclic carbonate were supplied by Matheson, Coleman & Bell.

Preparation of Materials (Continued)

(1) Materials - Activated "A" Carbon; Matheson, Coleman and Bell.

- Norit "Activated"; British Drug House.

- Fisher Adsorption Alumina; Fisher Scientific.

Other chemicals were also used; however, these are mentioned under the description of individual experiments.

(11) History of Polymer Samples - The samples of polyacrylonitrile except one were supplied by the Chemstrand Corporation. The weight average molecular weights were reported for each sample by the suppliers.

TABLE IX

<u>Sample*</u>	<u>M_v Reported</u>	<u>$[\eta]_{DMS} (gm/100 ml)^{-1}$</u>	<u>M_v'</u>
1....A-78880-A	200,000	2.19	198,000
2....A-78880-B	110,000	1.40	109,000
3....A-78880-C	70,000	0.81	52,600

The weight average molecular weights were determined in this laboratory from the intrinsic viscosities of each polymer sample measured in dimethylformamide. The M_v

* The code number used to designate the sample number was the same as that employed by the suppliers.

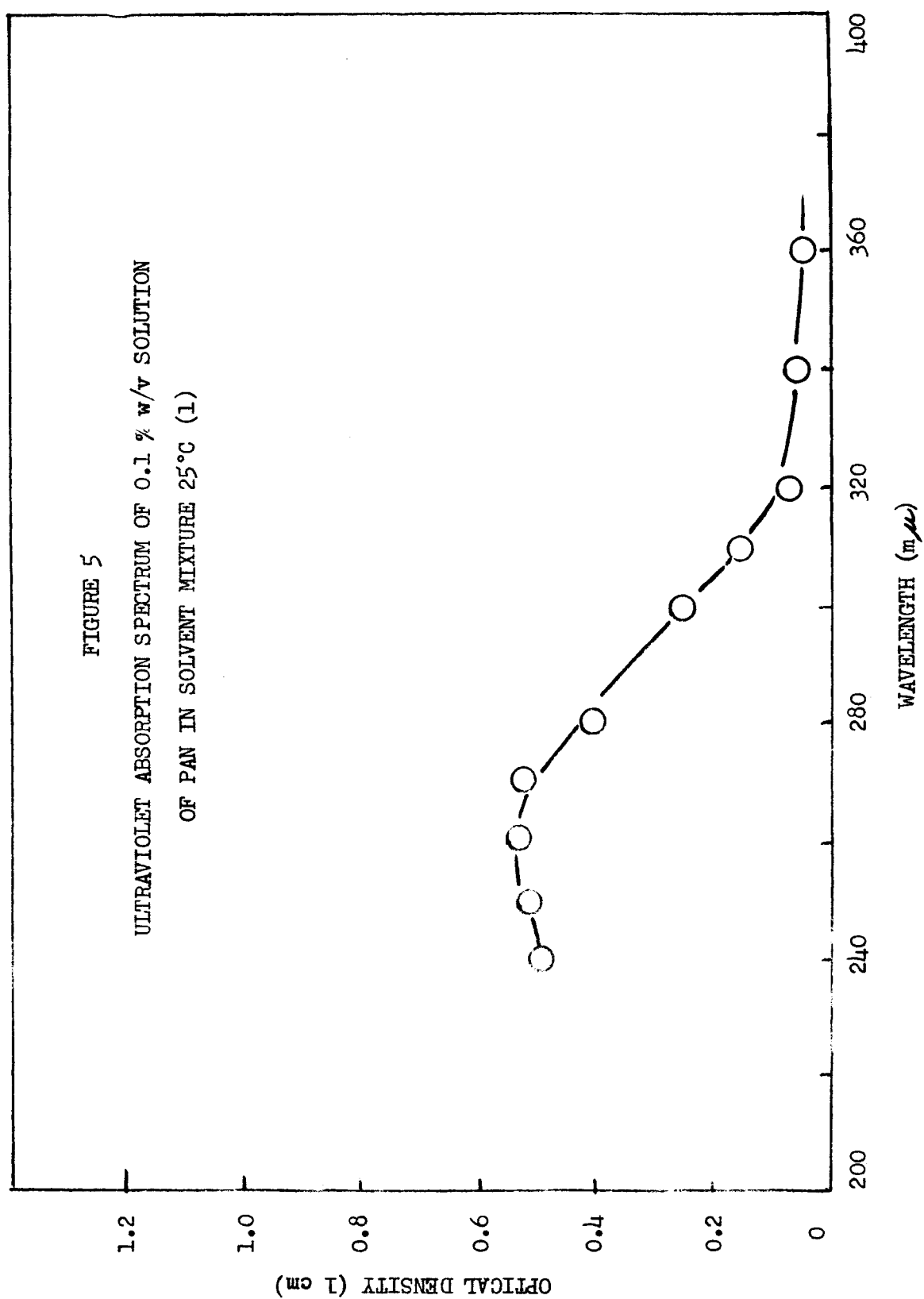
values correspond to twice the M_n values in Table V. The Cleland and Stockmayer equation was used to determine the weight average molecular weights (See Table III).

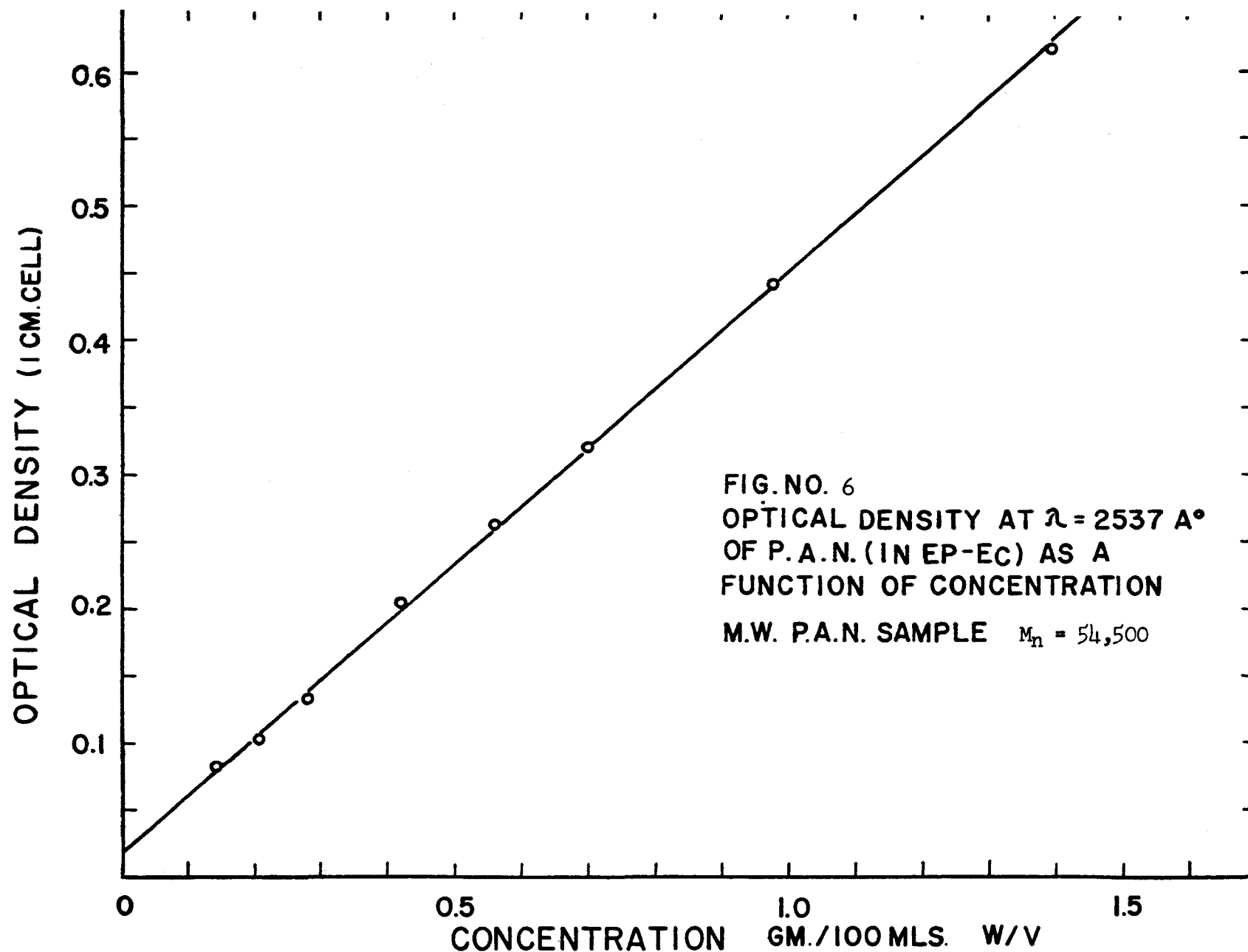
The difference between the reported weight average molecular weight and that determined in our laboratory is indicative of some abnormal characteristics of polymer sample 3. The abnormal behaviour of this polymer sample is illustrated in Chapter V.

Each polymer sample had an absorption maximum at 265 mμ, in their ultraviolet spectra (see Figure 5). The spectra were taken on solutions of the polymer dissolved in the ethylene carbonate - propylene carbonate solvent mixture. Figure 6 indicates that the polymer obeyed Beer's Law. The lamp, emitting energy of wave length 253.7 mμ., seemed ideal therefore for the degradation experiments.

(iii) Purification of the Solvent - The ethylene carbonate and 1,2 propanediol cyclic carbonate were purified by the methods suggested by Jellinek and Schluster (1, 13). Pritted glass filters and glassware cleaned with methanol were used in transferring the purified solvent components to prevent contamination.

The ethylene carbonate as supplied by the manufacturers absorbed all radiation below 2800 Å°. It was melted, and approximately 50 ml. of optically pure (acetone free) methanol for each kilogram of ethylene carbonate was





added. After crystallization proceeded (24 hrs), the mother liquor was drained off. Additional ethylene carbonate was frozen out and the process was repeated. The progress of purification was checked by measuring the ultraviolet absorption spectra of the carbonate in methanol. Four recrystallizations were found to be necessary for obtaining a satisfactory product. The ethylene carbonate was accepted to be of sufficient purity when an 80:20 mixture by weight of the material with methanol gave an optical density of less than 0.06 in a 1 cm. cell at 253.7 mμ. measured against distilled water as a standard. The resulting ethylene carbonate from recrystallization was dried under vacuum. The melting point after purification was 34-35°C.

The 1,2 propanediol cyclic carbonate also absorbed all radiation below 2600 Å°. It was purified by passing the material through columns of activated charcoal mixed with small amounts of Fisher adsorption alumina. The alumina helped to prevent channeling and increased the rate of flow through the columns. This constituted the only change in the method of purification from that used by Jellinek and Schluster (1). The use of activated charcoal alone did not give a product of good optical purity. Often, partially pure solvent increased in optical density when passed through a

freshly prepared column. Columns were discarded when they failed to lower the optical density of the cyclic carbonate.

It was also found that British Drug House Norit could be used with small amounts of alumina. In this case, the absorption of the material at 2537 \AA decreased at a much faster rate, and fewer columns were necessary. The absorption spectrum of the purified product is shown in Figure 7.

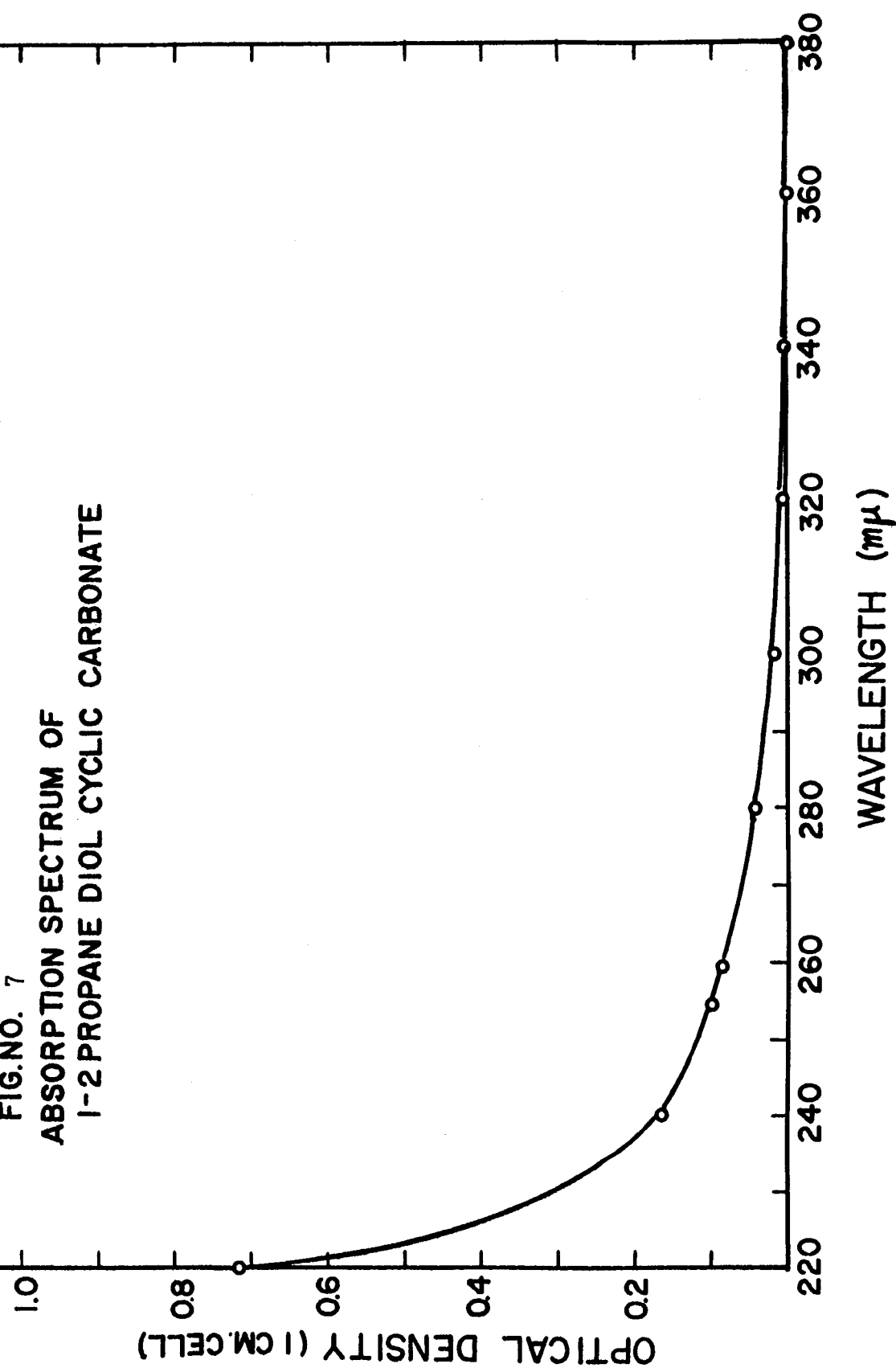
The resultant 80:20 mixture by weight of ethylene carbonate and 1,2 propane diol cyclic carbonate was dried in vacuum. The optical density (1 cm) at $253.7 \text{ m}\mu$ was 0.05 as shown in Figure 8.

Apparatus

The apparatus used in these present experiments was essentially the same as that employed in the previous work (13). Only a few alterations were made in the original setup. The 30 mm. low pressure mercury lamp was replaced by a 60 mm. lamp of similar design. The light source was placed as close as possible to the reaction vessel which gave maximum incident light intensity. The arrangement of the apparatus is well illustrated in Figure 9.

It consisted of the constant temperature bath of three and one-half gallons capacity. One of the glass plates was removed and in its place a brass plate was mounted. The brass plate had a circular hole of 5 cm. diameter across

FIG.NO. 7
ABSORPTION SPECTRUM OF
1-2PROPANE DIOL CYCLIC CARBONATE



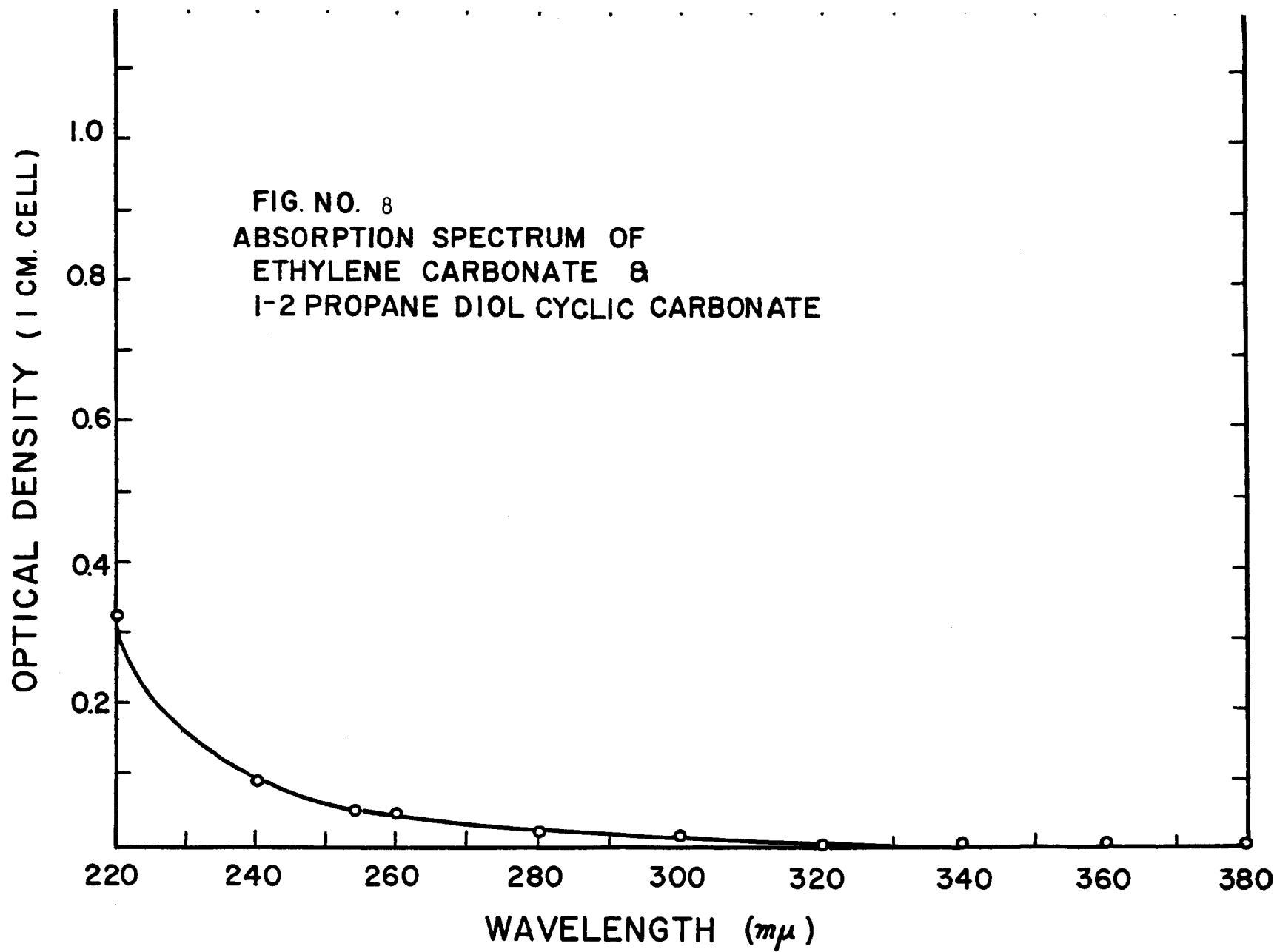
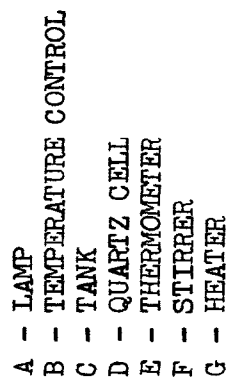


FIGURE 9



which a circular ultrasil quartz window (2 mm. thick, 7.7 cm. diameter) was secured by O-rings and by a brass frame screwed onto the brass plate. The tank was rigidly located on a steel base by four angle irons. This steel base was about twice as long as the tank and had an optical bench mounted on it at right angles to the tank exactly below the centre of the quartz window. This optical bench carried the light source and allowed an accurate alignment of the equipment. The reaction vessel and any other necessary equipment could be mounted along the entire length of the bath on a rail. The reaction vessel could be secured to the rail by suitable clamps and accurately positioned. The reaction vessel was placed in the water bath 1 cm from the quartz window. The 60 mm. lamp was 14.5 cm. from the centre of the supporting stand of the lamp to the brass wall plate of the tank. The distance between the lamp and reaction vessel was 3.0 cm. The bath was maintained at $25 \pm 0.05^{\circ}\text{C}$. by the usual arrangement of stirrer, heater, and relay.

Quartz Reaction Vessels

In the previous work (1) most of the reaction vessels had curved surfaces without plane parallel windows. In the work presented in this thesis, all vessels were cylindrical with plane polished ultrasil windows of 2 mm. thickness. See Figure 9. The diameter of the windows was 4 cm. and the length of the reaction vessels was 3 cm. I.D. The cells had a tubular stem of 10 cm. with a 19/38 $\frac{1}{8}$ male

joint. All cells were constructed of ultrasil quartz and were supplied by the Amersil and Pyrocell Companies. The light transmission of the quartz for a thickness of 1 cm. was nearly 100 per cent in the wave length region from 3000 to 2500 angstroms.

Hanovia 2537 Lamps

The lamps used in the degradation experiments were of the cold mercury vapour discharge type contained within a fused quartz envelope that transmits radiation almost completely at 2537 angstroms. The purpose of lamps of this type is to generate a sharply defined line spectrum of short wave length. The line most strongly emitted was at 2537 angstroms. This line represents about 95 per cent of the ultraviolet output of the tube. There were only traces of radiation of shorter wave length. Visible and infrared radiations were of a relatively low intensity as is evidenced by the low operating temperatures of these types of lamps.

The lamps were custom built by Engelhard Industries Incorporated, Newark, New Jersey, U.S.A. The lamps had a circular grid such that the area emitted a uniform path of rays from the nearly flat surface. Each lamp had its own alternating current power supply. A 60 ma. lamp was used in most experiments, and a 30 ma. lamp was used when the degradation experiments were carried out at

different intensities of the light source. The power supply is described in Chapter IV.

Viscometers

The course of the degradation was followed by measuring the intrinsic viscosities of undegraded and degraded polymer solutions. Sargent #100 Ostwald-Fenske Viscometers were used to determine all viscosity data.

Ultraviolet and Infrared Spectrophotometer

The ultraviolet absorption spectra for the purified products, and the polymer solutions were measured with a Beckman Spectrophotometer, Model DU. During later stages of the research project, the Bausch-Lomb Spectronic 505 recording spectrophotometer became available. Certain interesting experimental details were obtained in the region of 2160 angstroms with this instrument which could not be measured with the Beckman instrument.

Infrared spectra were determined with two types of instruments. Samples of degraded and undegraded material were sent to the Perkin Elmer Corporation for the determination of their spectra with the model 221-G Spectrophotometer. Most infrared spectra, however, were taken with the aid of the Beckman IR-5 spectrophotometer in the Chemistry Department.

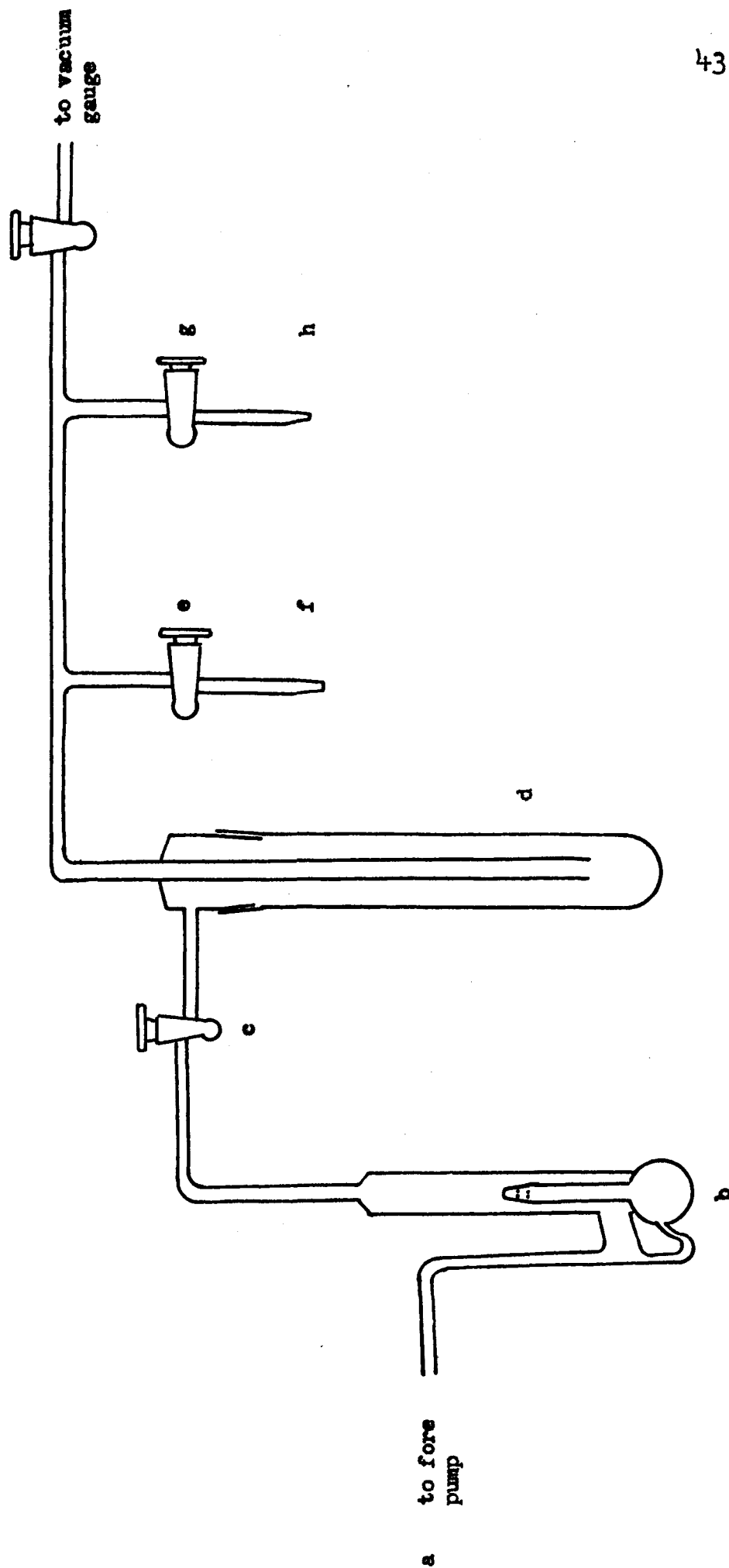
High Vacuum System

As the degradation of the polymer is greatly affected by the presence of oxygen in the reaction vessels, a high vacuum system was built to evacuate the reaction cells. The apparatus is shown in Figure 10.

It consisted of a mechanical fore pump (a), a mercury diffusion pump (b), a cold trap (c), a pressure gauge (d), two vacuum stopcocks (e and f), and two ground glass joints (g and h) to which the reaction cells could be attached. The quartz cells were connected with 19/38 outer joints to the vacuum line via pyrex adapters of 17 mm. O.D. having $\frac{3}{8}$ joints at each end. After the reaction cell was evacuated, it was sealed off under vacuum at a constriction in the adapter. After the cell was exposed to the ultraviolet radiation, it could be opened by breaking the pyrex tubing above the outer joint.

The reaction cells were evacuated by first freezing the solution in a liquid air bath and then connecting the cell to the vacuum line with the stopcock. The cells were evacuated for a half hour while in the liquid air bath and then shut off from the line at the stopcock. The solution was subsequently allowed to warm to room temperature during which time bubbles escaped from the solution. The liquid air bath was then placed around the cell and the cell again connected to the vacuum line. This

FIGURE 10
HIGH VACUUM SYSTEM



cycle was repeated until the bubbles stopped forming when the cells were warmed to room temperature. At this point, the cells were sealed off at the constriction in the adapter. They were then exposed to the UV radiation and the intrinsic viscosities measured.

CHAPTER IV

PRELIMINARY EXPERIMENTS

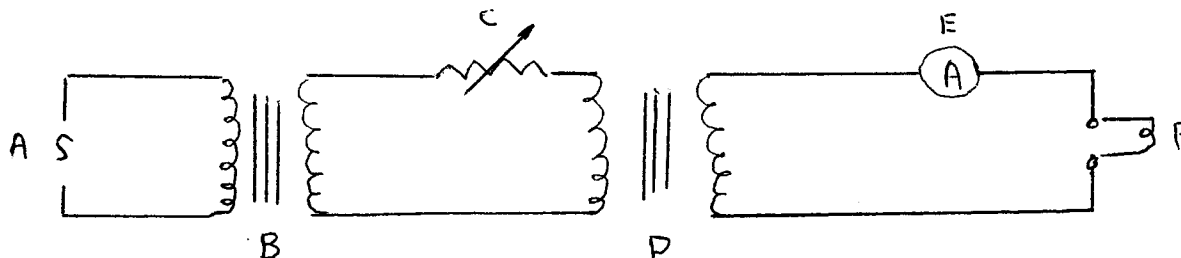
Before exact studies were carried out on the degradation of PAN in solution under (static) vacuum, preliminary experiments were performed on the polymer to determine the extent of the degradation after a certain period of time. Line current and voltage also had to be maintained so that a steady intensity of the light source was insured for all experiments.

A-C Power Supply

Heidt and Boyles (35) have determined the necessary requirements for the maintenance of constant intensity for a cold mercury lamp emitting energy of wave length 2537 angstroms. The main requirements were that the temperature of the lamp and the current through the lamp be kept constant. The power supplies used in this work were the same as those suggested by Heidt and Boyles and the manufacturers of our lamps (see Figure 11).

FIGURE 11

SCHEMATIC DIAGRAM OF THE LAMP CIRCUIT



The lamp (F) was connected to a high voltage transformer (D) delivering a current rating of 60 ma. The power to the transformer could be varied by a variac power supply (C) which was connected to the primary of the high voltage transformer. Constant voltage was maintained in all cases by connecting the lamp circuit to a Sola constant voltage transformer (B) of proper power rating.

The Sola constant voltage transformer is a static-magnetic voltage regulator. The output voltage is regulated within $\pm 1\%$ with primary voltage variations as great as 30%.

It was thus possible to maintain a constant current within 0.1 ma. for the lamp used. A Bach Simpson A.C. Milliametre (E) was inserted in the above circuit. After a two hour warming period, a current reading of 58.3 ma. was maintained for a period of 72 hours using the 60 ma. lamp. Periodic checks during each phase of the research work indicated no variation in the current.

The 30 ma. lamp, when inserted in its proper power supply circuit, gave a current reading of 28.1 ma. which did not vary after a two hour warmup period.

Lamp Temperature

The temperature of the lamps was checked with a Y.S.I. Thermistemp controller using a model 408 surface probe.

After each lamp had a two hour warmup period, the temperature probe was inserted in the lamp housings. For an

eight hour period the temperature of the 60 ma. lamp remained steady at $54.0 \pm 0.1^{\circ}\text{C}$. However, this was done when the room temperature was steady at 25°C . An increase in room temperature caused the lamp temperature to rise as high as 56.5°C ., and a decrease in room temperature caused the lamp temperature to decrease as low as 52°C . The 30 ma. lamp rose to a temperature of $54.0 \pm 0.1^{\circ}\text{C}$. after a two hour warmup period, but its temperature also fluctuated similarly.

The fact that the lamp temperature fluctuated with room temperature could not be considered as a fluctuation of the lamp intensity. Heidt and Boyles (35), in performing their experiments, kept the temperature constant by placing the lamp in a constant temperature bath. With an increase or decrease in the temperature of the room, undoubtedly, the temperature of the surroundings of the lamp would show a corresponding increase or decrease in temperature.

In order to determine the steadiness of the lamp intensity, a solution of polymer was degraded for 40 hours. This was done at different phases of the research work. The degree of degradation in terms of intrinsic viscosity measurements was constant within two per cent of the average. A 0.2 per cent polymer solution, whose intrinsic viscosity was initially $1.21 (\text{gr}/100 \text{ ml})^{-1}$, degraded to an intrinsic viscosity of $0.59 \pm 0.01 (\text{gr}/100 \text{ ml})^{-1}$.

As the 30 ma. lamp was used for only a very small phase of the work, the steady current through the lamp was considered a measure of the constant lamp intensity.

Measurement of Intrinsic Viscosity

The intrinsic viscosities of the polymer samples were obtained in the following manner. The flow time of a definite volume of polymer solution was measured in a viscometer. The specific viscosity at that particular concentration is defined as,

$$\eta_{sp} = \frac{t_s - t_0}{t_0}$$

where t_s is the flow time of the solution,

and t_0 is the flow time of the solvent.

The specific viscosity was measured at a number of concentrations for each sample. For each concentration the ratio η_{sp}/C was obtained, and plotted as a function of concentration C . The points η_{sp}/C defined a straight line which could be extrapolated to zero concentration. The intrinsic viscosity is defined as the limiting value of η_{sp}/C for zero concentration. Since η_{sp} is dimensionless, $[\eta]$ has the dimensions of concentration $^{-1}$. The concentration is expressed in gm./100 ml.

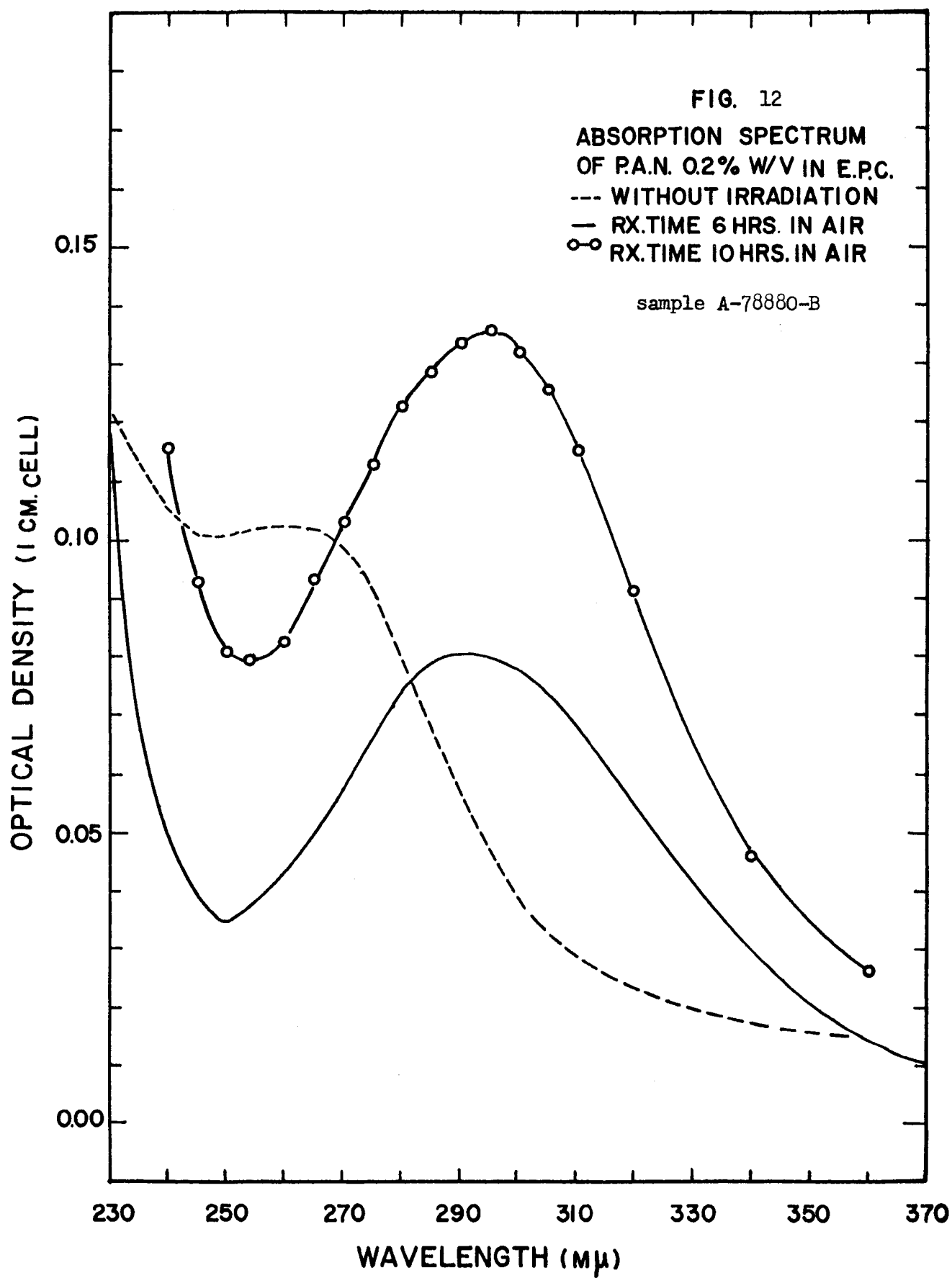
Degradation of PAN in Solution in the Presence of Oxygen

In most degradation experiments a polymer sample (A-78880-B) whose initial intrinsic viscosity was

$1.21 \text{ (gm./100 ml.)}^{-1}$ was used. In order to ascertain the extent to which the polymer degraded, a preliminary experiment was carried out on a 0.2 per cent w/v solution of PAN in the solvent mixture. Solutions were irradiated for periods of six and ten hours respectively in presence of air. The ultraviolet absorption spectra of the degraded and undegraded solutions were determined. The intrinsic viscosity decreased to 0.93 and 0.76 for the six and ten hour exposures, respectively. The absorption spectra are shown in Figure 12.

The experimental results indicate that the degradation proceeds slowly in terms of reduction of intrinsic viscosity. Since Jellinek and Schluter (1) had shown that the degradation was much faster in the presence of oxygen than in vacuum, it was to be expected that the degradation in vacuum would be very slow. The extent of degradation will be treated in more detail in Chapter V, where precise experiments will be presented.

One interesting observation at this point is that a new and definite peak appeared in the region of 2950 angstroms. Although this peak was not observed in the previous work, its increase was followed in all subsequent experimental work. It should be mentioned that Schluter obtained a shift in the absorption maximum at 2650 angstroms to 2950 angstroms for degradation of polymer samples having



a concentration of one per cent w/v PAN. However, this change was not followed during the course of his experiments.

Since the lamp intensity was much stronger than that previously used by Jellinek and Schnitzer (1), it was checked whether irradiation of the solvent mixture alone produced any change in its flow time and absorption spectrum. However, exposure of degassed samples failed to produce any changes.

It was reported by Jellinek and Schnitzer (1) that a dark reaction was observed after exposure of the PAN samples. For the concentration ranges studied in this work, the dark reaction could only be detected 24 hours after irradiation was stopped. As all intrinsic viscosity measurements were carried out within one hour after exposure, the dark reaction was considered negligible.

Number Average Molecular Weight - Intrinsic Viscosity Relationship

The intrinsic viscosity data as determined by Jellinek and Schnitzer (1) was confirmed. This led to the subsequent relationship developed from the data of Table IV.

$$[\eta] = 2.65 \times 10^{-3} M_n^{0.56}$$

This relationship was used to determine all number average molecular weights and chain lengths.

CHAPTER V

EXPERIMENTAL RESULTS

Degradation of PAN in Solution as a Function of Concentration

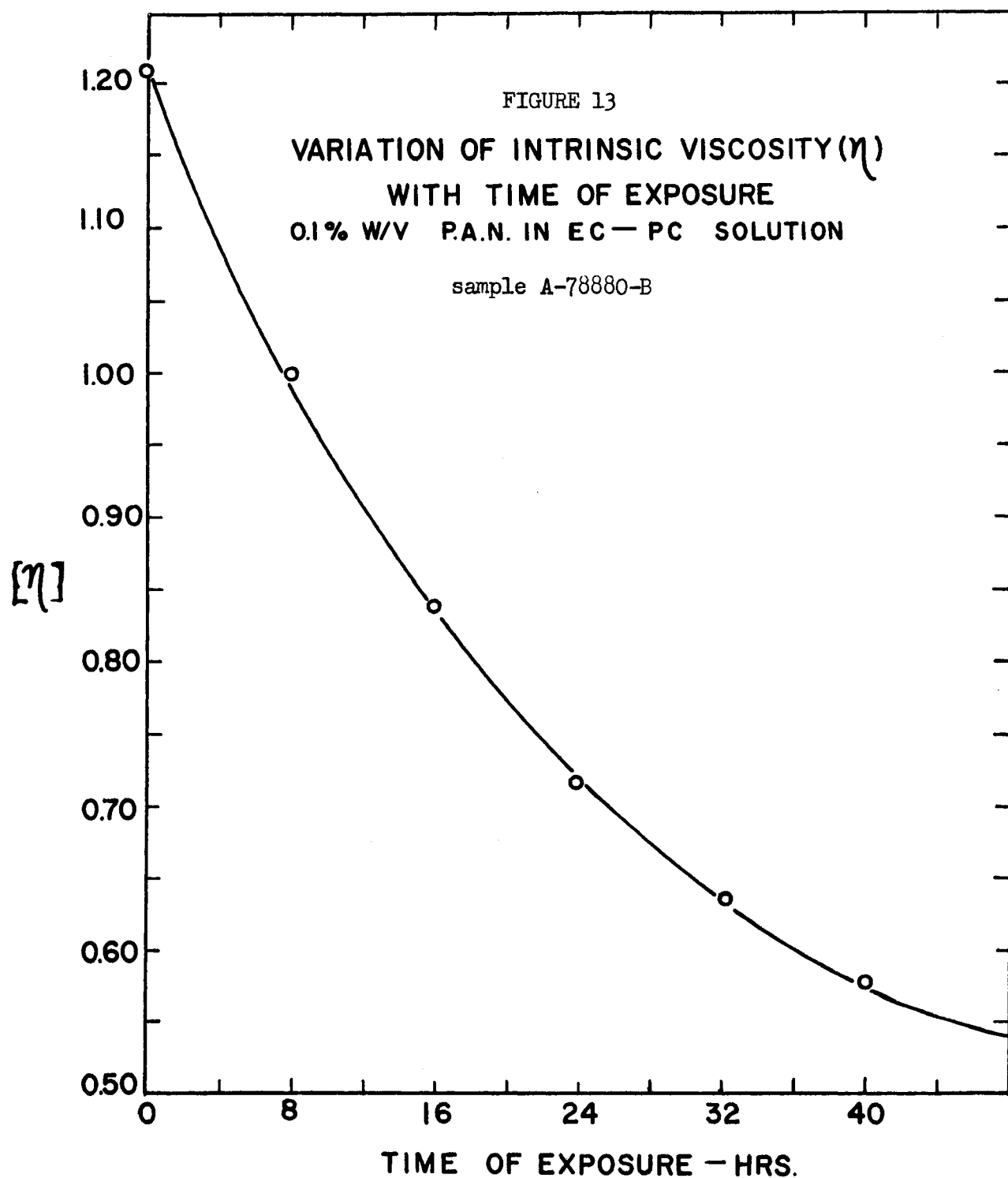
It is well to mention here that all degradation experiments were carried out with dilute and degassed polymer solutions.

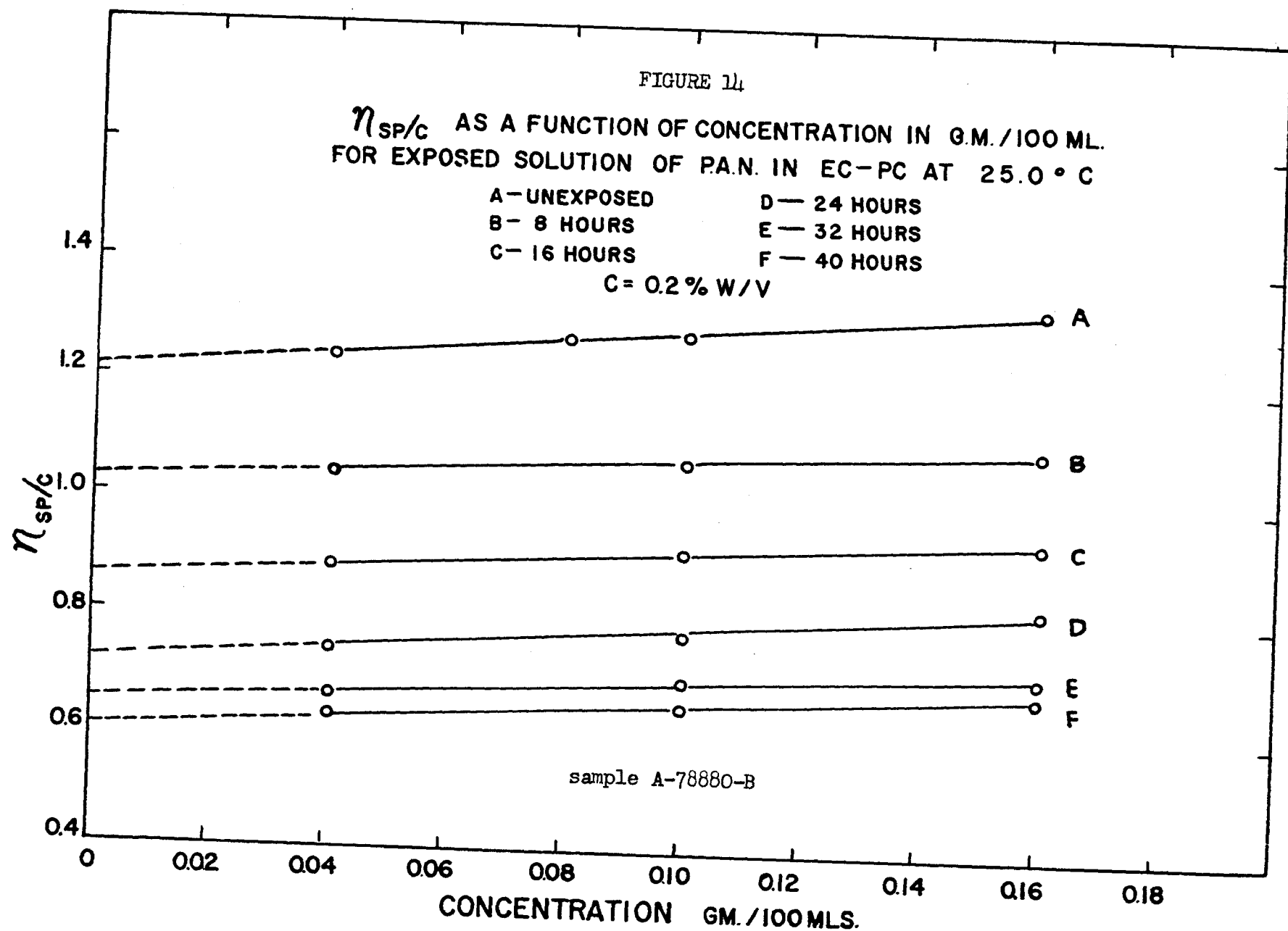
Table IX illustrates the decrease in intrinsic viscosities of degraded polymer samples*. Changes in optical density at 2537 angstroms and 2950 angstroms, and number average chain lengths, P_n , are also listed.

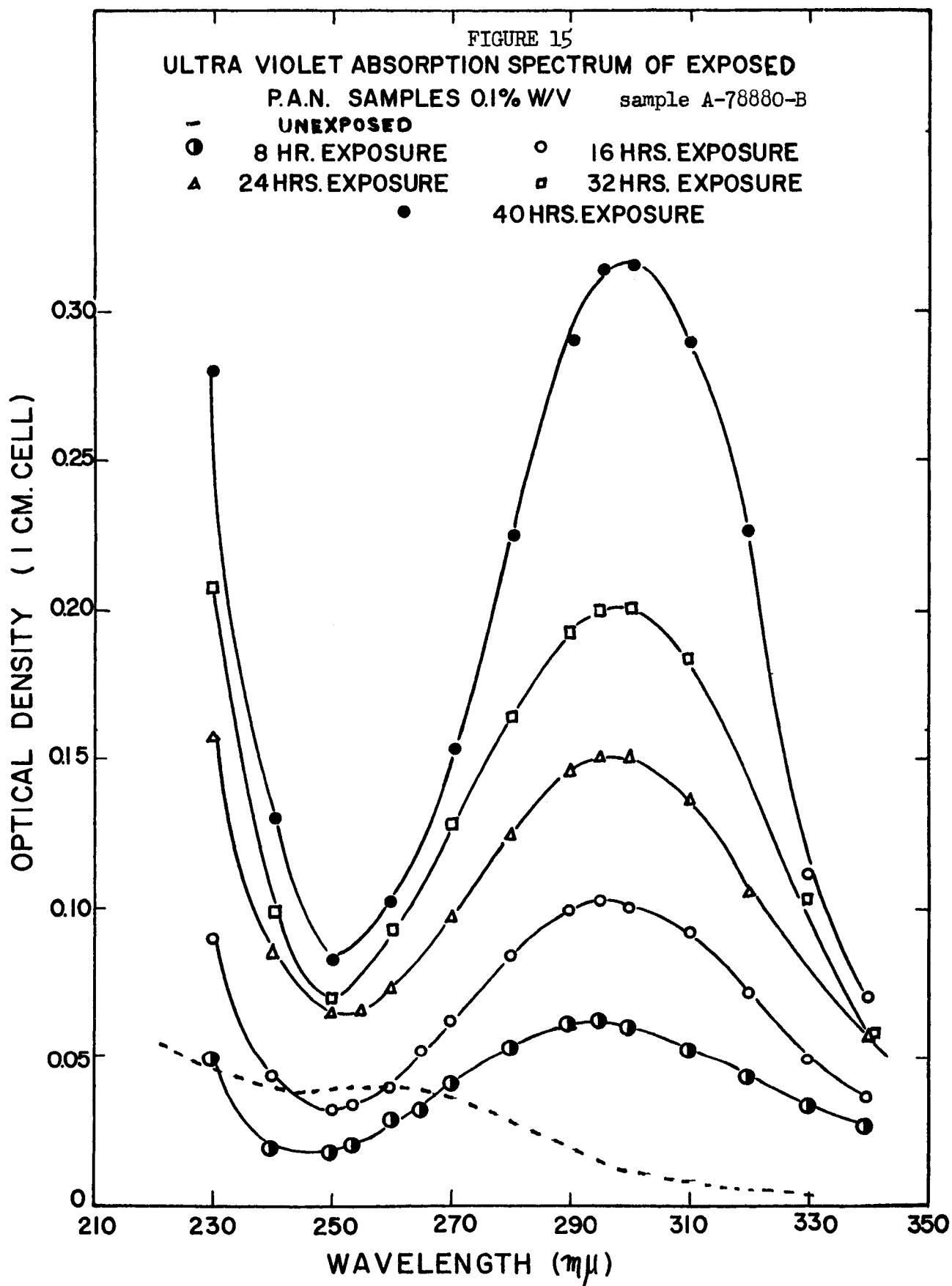
Figure 13 shows the intrinsic viscosities as a function of irradiation time for a 0.2 per cent solution of PAN, sample A-78880-B. Figure 14 shows the relevant straight lines for the determination of the intrinsic viscosities for a 0.2 per cent solution. All slopes are practically the same, only showing a slight increase with increasing intrinsic viscosity. The corresponding slopes for the solutions of original concentrations 0.1 per cent and 0.4 per cent w/v were also practically the same.

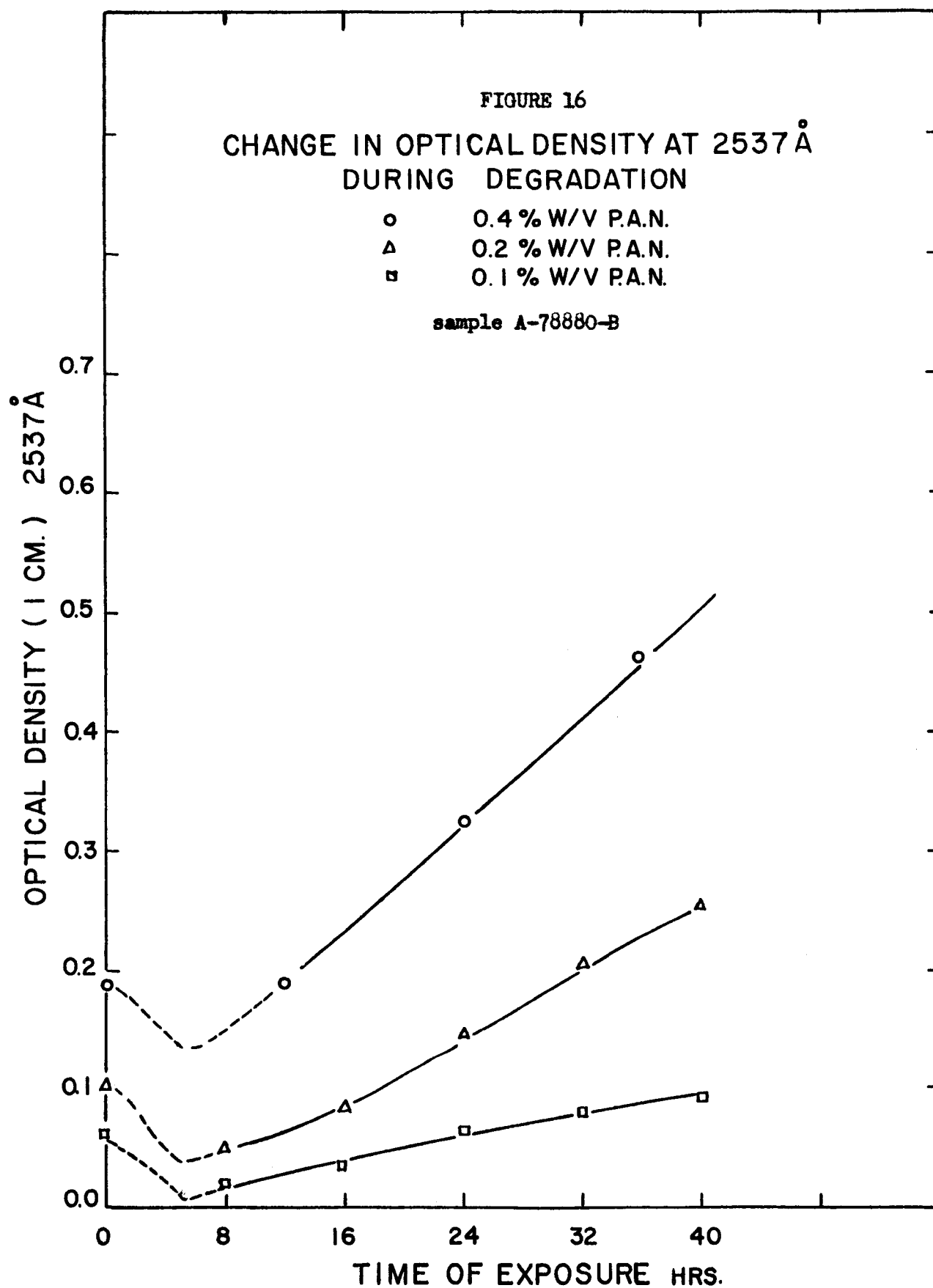
Figure 15 illustrates the change in absorption spectra of the 0.1 per cent w/v polymer solutions. Figure 16 and Figure 17 illustrates the change in optical density at

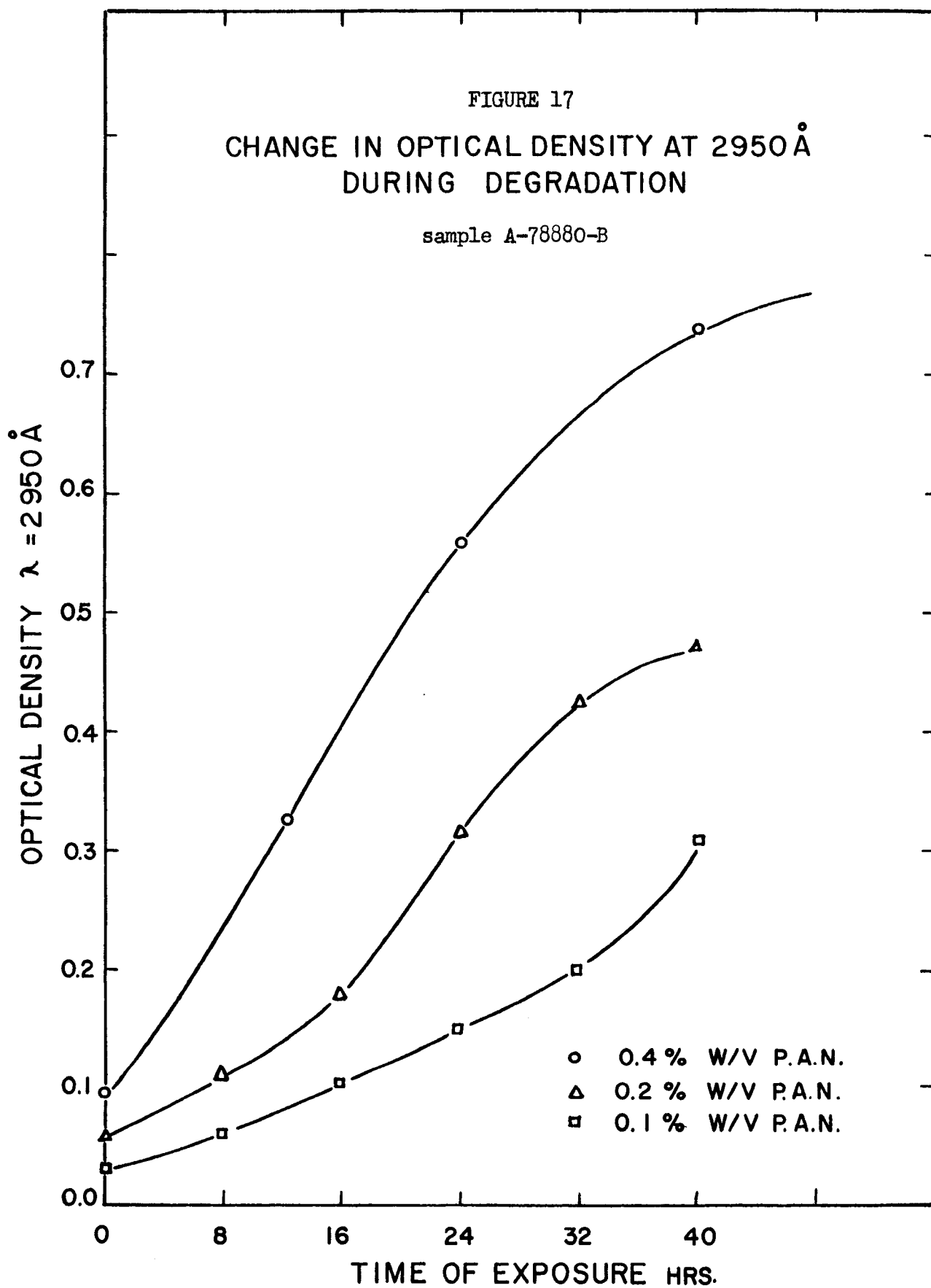
* The degradation of PAN in solutions as a function of concentration and chain length were performed using an incident light intensity of 2.58×10^{17} quanta/sec. per cell window. The determination of light intensities in terms of quanta will be discussed later.











2950 and 2537 angstroms as a function of time.

It should be mentioned that for degradation of the 0.4 per cent w/v solution, a gradual yellowing took place. The solution also appeared to fluoresce; this fluorescence being located mainly in the front part of the cell. This became more marked with increasing time of exposure.

TABLE X

PHOTODEGRADATION OF POLYACRYLONITRILE IN VACUUM AS A FUNCTION OF
CONCENTRATION IN 60:20 ETHYLENE CARBONATE-PROPYLENE CARBONATE

AT 25°C.

SAMPLE A-70880-B

<u>Concentration 0.15 w/v</u>			<u>Rate Constant $6.57 \times 10^{-5} \text{ hr}^{-1}$</u>		
<u>t(hrs)</u>	<u>[η]</u>	<u>P_t</u>	<u>(1/P_t)$\times 10^3$</u>	<u>Opt. Density (1cm) 2950A</u>	<u>Opt. Density (1cm) 2537A</u>
0	1.21	1030	0.97	0.037	0.060
8	1.00	752	1.33	0.063	0.020
16	0.84	552	1.81	0.103	0.034
24	0.72	420	2.38	0.149	0.065
32	0.64	340	2.94	0.201	0.080
40	0.53	286	3.50	0.315	0.090

<u>Concentration 0.25 w/v</u>			<u>Rate Constant $6.57 \times 10^{-5} \text{ hr}^{-1}$</u>		
0	1.21	1030	0.97	0.060	0.100
8	1.03	794	1.26	0.112	0.050
16	0.86	575	1.74	0.180	0.076
24	0.72	420	2.38	0.320	0.150
32	0.65	350	2.86	0.425	0.205
40	0.60	304	3.29	0.470	0.255

<u>Concentration 0.4% w/v</u>			<u>Rate Constant $6.57 \times 10^{-5} \text{ hr}^{-1}$</u>		
0	1.21	1030	0.97	0.09	0.180
12	0.92	640	1.56	0.326	0.190
24	0.72	420	2.38	0.560	0.325
36	0.65	350	2.86	0.740	0.466

Degradation of PAN in Solution for Different Initial Chain Lengths

Two samples (A-78880-A, A-78880-C) of different initial chain lengths were also degraded. The degradation of polymer samples of different molecular weights should certainly indicate whether or not this particular physical property of the polymer influenced the degradation in any way.

Table XI below indicates that sample A-78880-A followed the same type of degradation as sample A-78880-B. Sample A-78880-C of very low molecular weight did not degrade in the usual manner, but seemed to increase in molecular weight. One other feature of this sample was, that the polymer sample did not have a definite absorption maximum at 2950 angstroms, but showed a maximum at approximately 2850 angstroms. It was also noticed that the polymer solution turned distinctly yellow during the degradation. The sample also fluoresced to a very high degree as the exposure times were increased. There is no explanation for the abnormal behaviour of sample A-78880-C. One can only surmise that the difference in the measured values of the weight average molecular weights (see Table V) for this sample may indicate the presence of impurities.

The degradations of the polymer samples were carried out at a concentration of 0.1% w/v. The degradation of the sample whose initial intrinsic viscosity was

TABLE XI

DEGRADATION OF POLYACRYLONITRILE IN VACUUM AS A FUNCTION OF THE ORIGINAL CHAIN LENGTH IN 80:20 ETHYLENE CARBONATE-PROPYLENE CARBONATE AT 25°C. (ALL CONCENTRATIONS 0.1% W/V)

<u>$[\eta] = 1.21$</u>		<u>Rate Constant $6.57 \times 10^{-5} \text{ hr}^{-1}$</u>			
<u>t(hrs)</u>	<u>$[\eta]$</u>	<u>P_t</u>	<u>$(1/P_t) \times 10^3$</u>	<u>Opt. Density (1 cm) 2950 Å</u>	<u>Opt. Density (1 cm) 2537 Å</u>
0	1.21	1030	0.97	0.037	0.060
8	1.00	752	1.33	0.063	0.020
16	0.84	552	1.81	0.103	0.034
24	0.72	420	2.38	0.149	0.065
32	0.64	340	2.94	0.201	0.080
40	0.58	286	3.50	0.315	0.090

<u>$[\eta] = 1.65$</u>		<u>Rate Constant 6.05×10^{-5}</u>			
<u>t(hrs)</u>	<u>$[\eta]$</u>	<u>P_t</u>	<u>$(1/P_t) \times 10^3$</u>	<u>Opt. Density (1 cm) 2950 Å</u>	<u>Opt. Density (1 cm) 2537 Å</u>
0	1.65	1886	0.53	0.030	0.048
8	1.33	1305	0.77	0.057	0.013
16	1.06	840	1.19	0.118	0.021
24	0.88	599	1.67	0.142	0.055
32	0.77	472	2.12	0.193	0.072
40	0.69	389	2.57	0.237	0.090

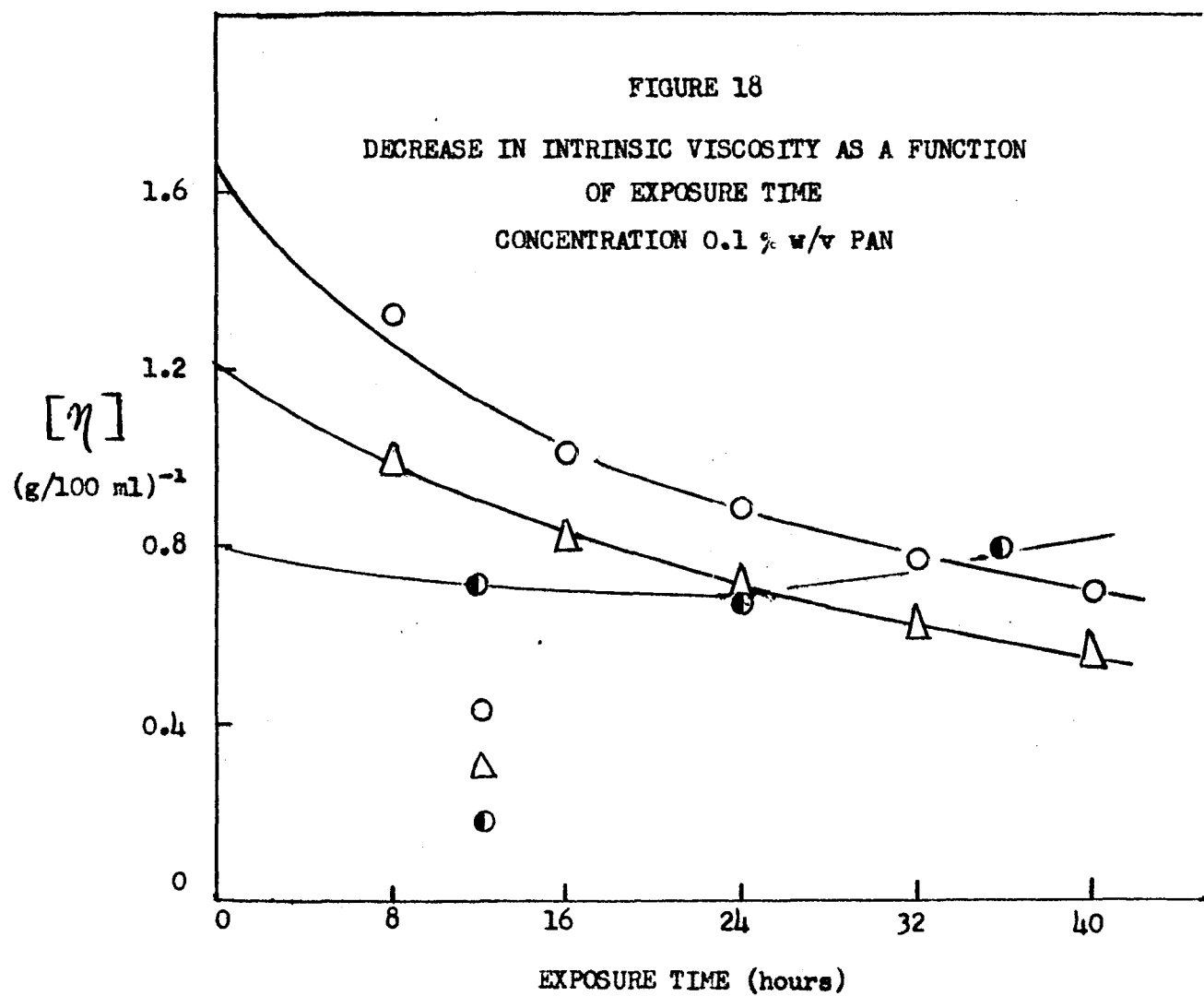
<u>$[\eta] = 0.78$</u>		<u>Opt. Density (1 cm) 2850 Å</u>			
<u>t(hrs)</u>	<u>$[\eta]$</u>	<u>P_t</u>	<u>$(1/P_t) \times 10^3$</u>	<u>Opt. Density (1 cm) 2950 Å</u>	<u>Opt. Density (1 cm) 2537 Å</u>
0	0.78	483	2.07	0.043	0.079
12	0.74	441	2.27	0.247	0.230
24	0.72	420	2.38	0.381	0.356
36	0.80	505	1.98	0.475	0.432

1.21 (g/100 ml)⁻¹ is also included in the table for convenience. Figure 18 illustrates the change in intrinsic viscosity for the three samples.

The Degradation of PAN in Solution at Different Incident Light Intensities

The degradation was also studied at three different intensities. This was achieved by placing the 60 ma. lamp 5.5 cm. from the reaction vessel, and by replacing the 60 ma. lamp with a 30 ma. lamp at a distance of 8.5 cm. from the vessel. The radiation incident to the reaction vessel was measured using the uranyl oxalate-oxalic acid actinometer (34). The actinometer has a known quantum yield of 0.65 molecules of oxalate decomposed per absorbed quantum of energy of wave length 2537 angstroms. The oxalate in the system was titrated with potassium permanganate in the usual manner. This gave an excellent means for the determination of the incident light intensity.

(1) Preparation of Uranyl Oxalate - Uranium trioxide was heated in concentrated sulphuric acid until all the oxide had been dissolved. The solution was cooled and filtered through a sintered glass crucible. Some of the uranyl sulphate crystallized on cooling. Any uranyl sulphate in the crucible was dissolved with hot distilled water and washed through the sintered glass crucible. The aqueous solution, which remained in the filtrate, was heated to fuming and then allowed to cool when the uranyl sulphate crystallized out. The remaining liquid was filtered through



sintered glass crucibles and the sulphate left in the crucibles was washed with distilled water. The remaining uranyl sulphate was then dissolved in boiling water to obtain a highly concentrated solution. A saturated solution of oxalic acid was made in boiling water and transferred to the hot uranyl sulphate solution. The uranyl oxalate precipitated out and was obtained by decanting the remainder of the solution. The resulting uranyl oxalate was washed several times with distilled water, which was continued until approximately one-third of the oxalate had dissolved. The remaining material was collected on a fritted glass filter and placed in a vacuum dessicator until constant weight was obtained (24 hours). The uranium oxide was made available to Essex College for research purposes by the Atom Energy of Canada. The oxalic acid was the dihydrate, analar grade from British Drug House. The oxalic acid was recrystallized from distilled water before use.

(11) Incident Light Intensity - A solution was made of 0.012 moles of uranyl oxalate and 0.06 moles of oxalic acid per litre of solution and the same reaction cells, which had been used for the photodegradation, were filled with this solution. Each reaction vessel held 33.00 ml. of actinometer solution. The reaction vessels containing the actinometer solution were placed in the tank and secured to the rail so that they were in the same position as the reaction vessels when they contained polymer

solution. They were exposed to the ultraviolet radiation for 10 minute periods. This experiment was repeated several times and for different light intensities.

The amount of oxalate decomposed during irradiation was determined from the difference of amounts of permanganate required to titrate the actinometer solution before and after exposure to the lamp source. The titrations were performed in the usual manner in acid media at approximately 80°C. The number of incident quanta could then be determined from the following relationship:

$$L = \frac{n N}{0.65 \Delta t}$$

where L is the number of incident quanta/sec., N is Avogadro's number, n is the number of moles of oxalate decomposed, Δt is the irradiation period in seconds and 0.65 is the quantum yield at 254 mμ. (33).

TABLE XII

DETERMINATION OF INCIDENT LIGHT INTENSITY

AMOUNT OF 0.0849 N KMnO_4 IN ML. REQUIRED TO TITRATE 25 ML.
OF ACTINOMETER SOLUTION

Intensities	I_1	I_2	I_3
Before Exposure	32.11	32.11	32.11
After Exposure (10 min)			
Test I	29.11	30.16	31.41
Test II	29.12	30.18	31.40
Volume Difference	$3.00 \pm .02$	$1.94 \pm .02$	$0.71 \pm .02$
Total Volume held by Reaction Vessel was 33.00 ml.			
Hence Corrected Volume Difference was:			
	$3.96 \pm .02$	$2.56 \pm .02$	$0.94 \pm .02$
Quanta absorbed/sec. for Reaction Vessel	2.58×10^{-17}	1.67×10^{-17}	0.61×10^{-17}

(iii) Degradation in Solution at DifferentIncident Light Intensities - The samples

had been degraded previously using an incident light intensity I_1 . The results of the degradation of the 0.1% solution at intensity I_1 are included with those degraded at incident intensities I_2 and I_3 . All samples degraded and given in Table XII had an initial intrinsic viscosity of $1.21 (\text{gm}/100 \text{ ml})^{-1}$.

TABLE XIII

DEGRADATION OF POLYACRYLONITRILE IN VACUUM AS A FUNCTION OF
 INCIDENT INTENSITY IN 80:20 BENZENE CARBONATE-PROPYLENE
 CARBONATE AT 25°C. (ALL CONCENTRATIONS 0.1% W/V)
 SAMPLE A-70880-B

<u>Intensity I₁</u>		<u>Rate Constant $6.57 \times 10^{-5} \text{ hr}^{-1}$</u>			
<u>t(hrs)</u>	<u>$[\eta]$</u>	<u>P_t</u>	<u>$(1/P_t) \times 10^3$</u>	<u>Opt. Density (1 cm) 2950 Å</u>	<u>Opt. Density (1 cm) 2537 Å</u>
0	1.21	1030	0.97	0.037	0.06
8	1.00	752	1.33	0.063	0.020
16	0.84	552	1.81	0.103	0.034
24	0.72	420	2.38	0.149	0.065
32	0.64	340	2.94	0.201	0.080
40	0.58	286	3.50	0.315	0.090

<u>Intensity I₂</u>		<u>Rate Constant $3.92 \times 10^{-5} \text{ hr}^{-1}$</u>			
<u>t(hrs)</u>	<u>$[\eta]$</u>	<u>P_t</u>	<u>$(1/P_t) \times 10^3$</u>	<u>Opt. Density (1 cm) 2950 Å</u>	<u>Opt. Density (1 cm) 2537 Å</u>
0	1.21	1030	0.97	0.037	0.06
8	1.05	820	1.22	0.055	0.019
16	0.93	658	1.52	0.075	0.026
24	0.82	529	1.89	0.112	0.038
32	0.74	441	2.27	0.143	0.058
40	0.68	379	2.64	0.176	0.073

<u>Intensity I₃</u>		<u>Rate Constant $1.52 \times 10^{-5} \text{ hr}^{-1}$</u>			
<u>t(hrs)</u>	<u>$[\eta]$</u>	<u>P_t</u>	<u>$(1/P_t) \times 10^3$</u>	<u>Opt. Density (1 cm) 2950 Å</u>	<u>Opt. Density (1 cm) 2537 Å</u>
0	1.21	1030	0.97	0.037	0.06
12	1.10	893	1.12	0.048	0.012
24	1.00	752	1.33	0.072	0.020
36	0.91	633	1.58	0.107	0.030

Preparation and Degradation of a Polymer Sample

A polymer sample was prepared to determine whether or not the history of the polymer sample would affect the degradation process. The method used for the polymerization was forwarded by Leighton H. Peebles Jr. of the Chemstrand Corporation. Their research had indicated that it was possible to "prepare very clean samples of polyacrylonitrile of good colour, little or no gel, and a known molecular weight distribution of 2.0 weight to number average molecular weight ratio by polymerization of acrylonitrile in solution". The following method was adopted for the polymerization:

(1) Polymerization of Acrylonitrile -

Acrylonitrile supplied by Eastman-Kodak was washed with 3N sulphuric acid, 3N sodium carbonate, and water, respectively. It was dried with calcium chloride and distilled twice at atmospheric pressure, the first and last fractions being discarded. Ethylene carbonate was used as the solvent medium and it was purified by the method adopted for the preparation of the solvent mixture. The ethylene carbonate was melted and transferred to a 25 ml quartz reaction vessel. Eastman-Kodak azobisisobutyronitrile, the initiator for the polymerization, was added to the ethylene carbonate to give a concentration of 0.0135 molar (36). The reaction vessel was then degassed on the vacuum line in the usual

manner. Acrylonitrile was added to give a concentration of 0.0538 molar ($3\frac{1}{2}$) and the mixture was frozen in a liquid air bath and evacuated on the vacuum line. While under vacuum (static), the reaction vessel was submerged in a water bath at 50°C. When solution was affected, the bath temperature was raised to 60-65°C. and the reaction was allowed to proceed for 45 minutes.

When the reaction period was complete, the vessel was removed from the bath and the vacuum line, and the contents poured slowly into well-stirred methanol which was optically pure. The polymer, which precipitated in the methanol, was collected on fritted glass filters and washed several times with methanol. The samples were then added to British Drug House - Analar ether and refluxed on a steam bath for one hour at atmospheric pressure. After refluxing with ether, the polymer was again filtered off. The polymer samples were then washed, refluxed, filtered, and again washed with methanol. Refluxing the material in methanol was repeated to ensure that a clean polymer was obtained. After collecting the polymer on fritted glass filters and washing with methanol, the PAN samples were placed in a vacuum oven at 40°C. until constant weight was obtained.

The polymer sample was used in subsequent degradation experiments. The intrinsic viscosity was

measured in the two solvents DMF and EC-PC:

<u>Intrinsic Viscosity</u> <u>($\text{cm}^3/100 \text{ ml})^{-1}$</u>	<u>Number Average Molecular Weight</u> <u>Cleland Stockmayer Equation</u>
0.50 in DMF solvent	13,800
0.54 in EC-PC solvent	13,400

0.1% w/v of the polymer in EC-PC solvent gave a different ultraviolet absorption spectrum than that for the samples obtained from the Chemstrand Corporation. A distinct band appeared at 216 m μ . and the usual 265 m μ . absorption was much higher (see Figure 19).

(ii) Degradation of Polymer Sample - The new sample was degraded as before using the maximum light intensity I_1 . The results of the degradation of a 0.1% w/v solution are given in Table XIV.

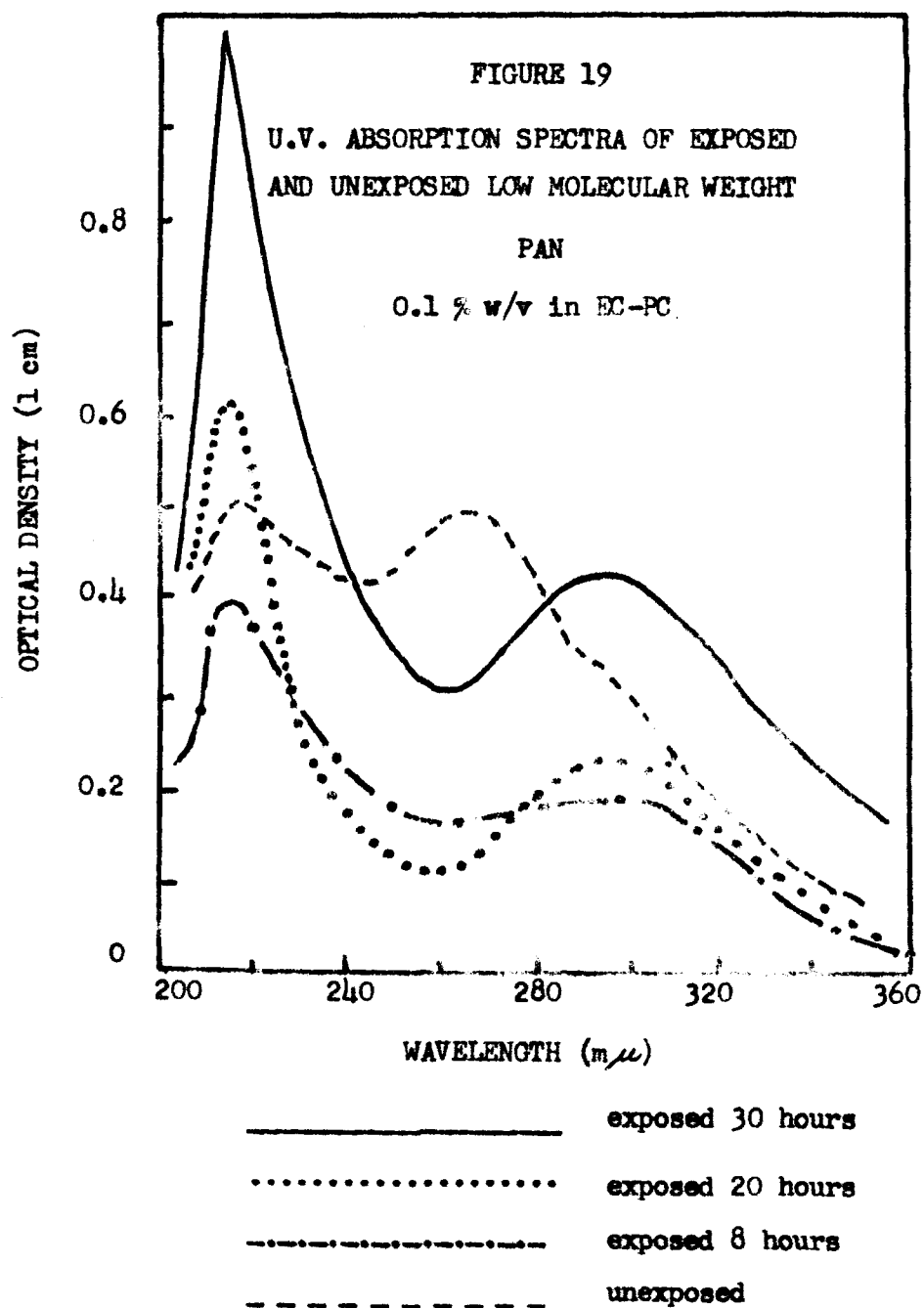
TABLE XIV

DEGRADATION OF PREPARED SAMPLE

(CONCENTRATION 0.1% W/V)

<u>t(hrs)</u>	<u>$[\eta]$</u> <u>($\text{cm}^3/100 \text{ ml})^{-1}$</u>	<u>P_t</u>	<u>$1/P_t \times 10^3$</u>	<u>Opt. Den.</u> <u>(216 mμ)</u>	<u>Opt. Den.</u> <u>(265 mμ)</u>	<u>Opt. Den.</u> <u>(295 mμ)</u>
0	0.54	252	3.97	0.492	0.243	0.484
8	0.50	219	4.56	0.412	0.207	0.190
20	0.44	174	5.74	0.619	0.243	0.110
30	0.41	153	6.54	0.921	0.412	0.325

Rate Constant $9.6 \times 10^{-5} (\text{hr})^{-1}$

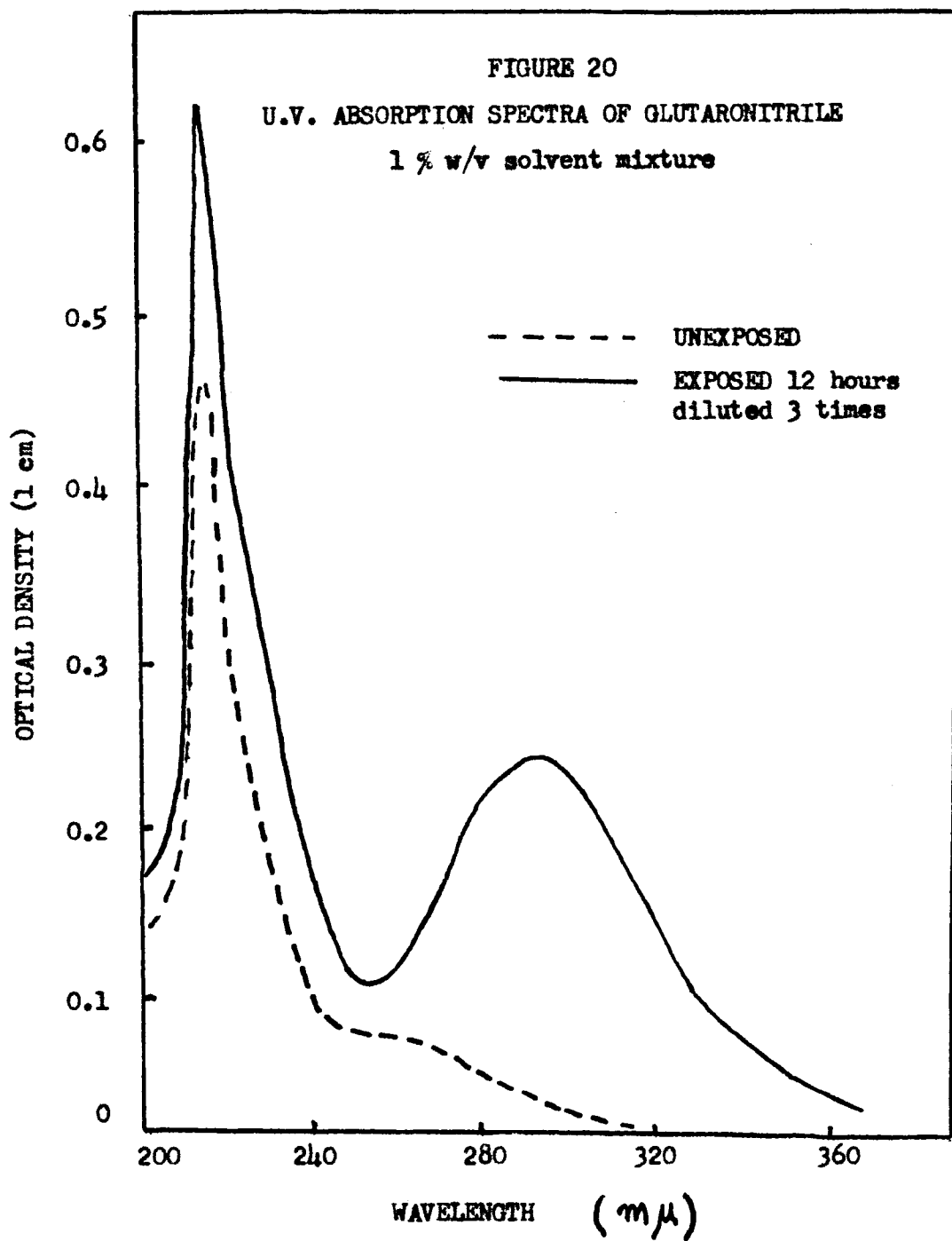


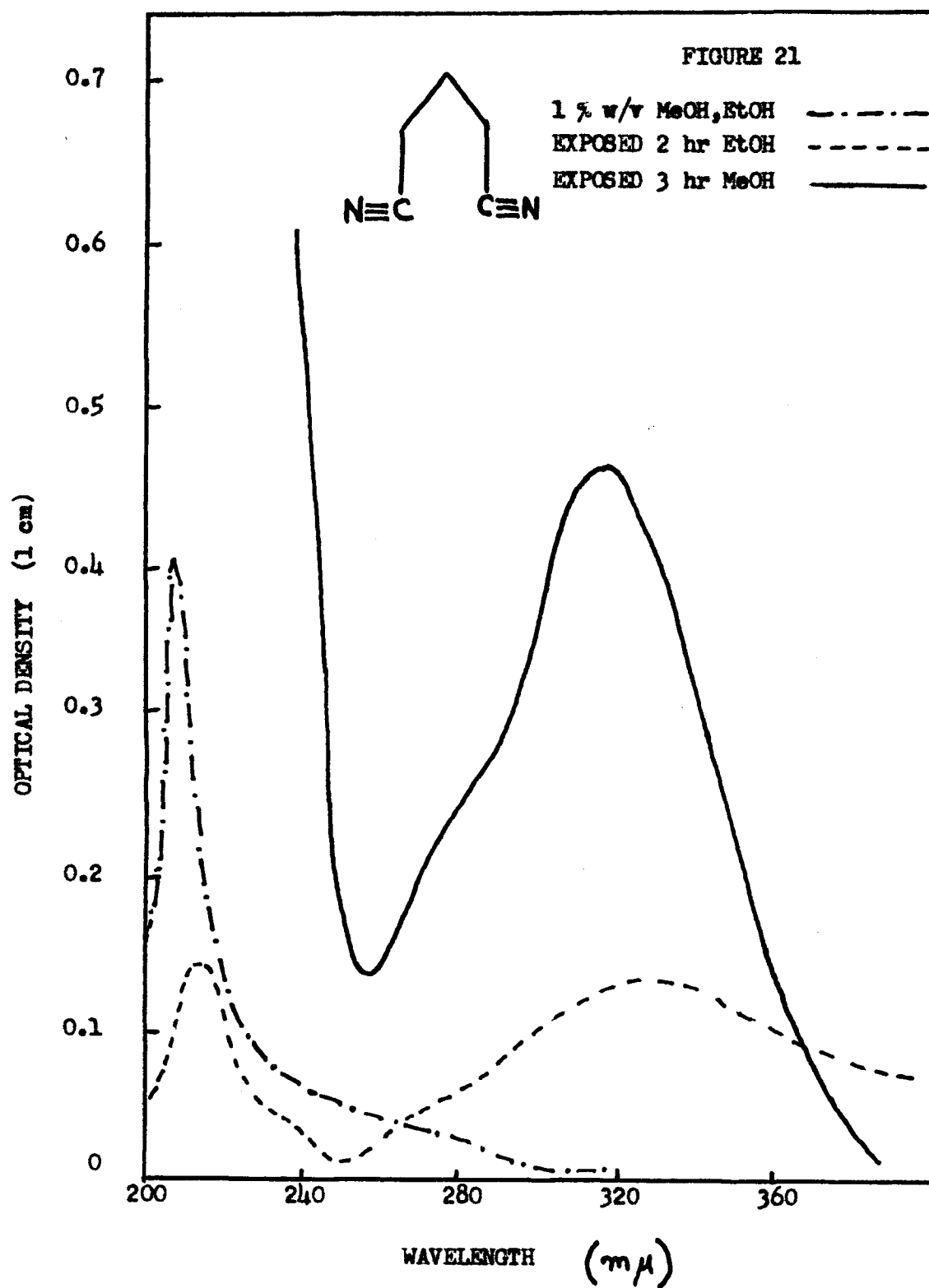
Other observations which were made during the degradation were as follows:

The absorption of 216 mμ decreased in the beginning of the degradation as illustrated by the sample degraded for eight hours (see Figure 19). The absorption then rose rapidly as did the absorption at 295 mμ. The absorption at 265 appeared to decrease rapidly. The degradation of this sample is compared to the degradation of the Chemstrand samples in Chapter VI.

Photolysis of Model Compound

A model compound, glutaronitrile, was exposed to the ultraviolet source with the hope of obtaining information which would be valuable in determining the structural unit responsible for the increase in absorption maximum of the polymer at 2950 angstroms. The glutaronitrile, $(\text{CH}_2)_3$ with CH groups at the ends, which has a basic structure similar to that of the polymer, was dissolved in three different solvents: the solvent mixture, methanol, and ethanol. When the sample 1 per cent w/v in the solvent mixture was exposed to radiation in vacuum an absorption maximum appeared at 290 mμ, (see Figure 20). At the same time the absorption maximum at 216 mμ appeared to increase. It should be mentioned that the absorption spectra were determined using the Bausch-Lomb Spectronic (505). The exposure of glutaronitrile in the solvents ethanol and methanol gave quite different results as illustrated in Figure 21. This





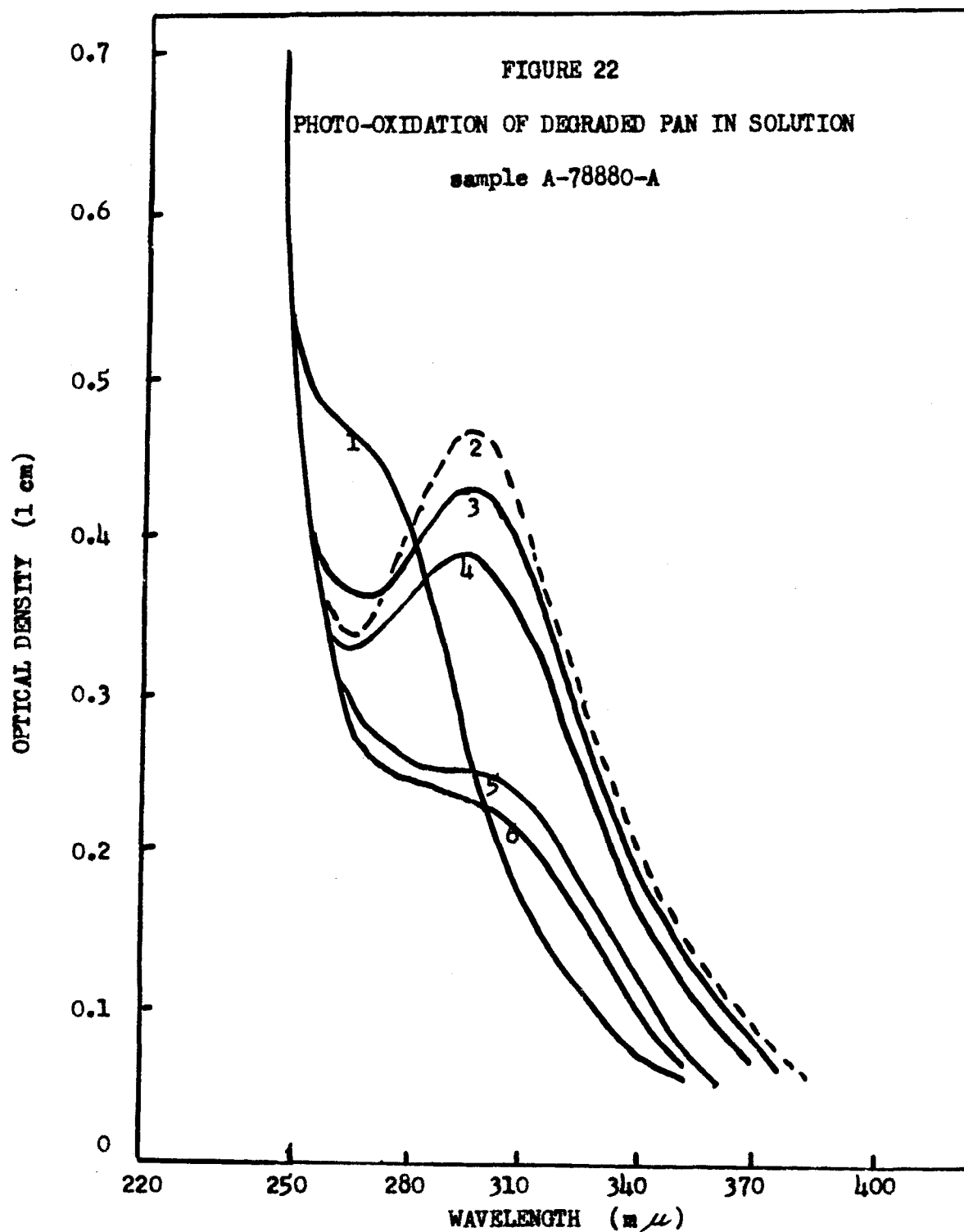
behaviour could not be accounted for.

The fact that the glutaronitrile had an absorption at 216 m μ , and an absorption in approximately the same position as that of the polymer in the region 265 m μ , prompted a re-analysis of the ultraviolet absorption spectra of the polymer sampler obtained from the Chemstrand Corporation.

Re-Analysis of Ultraviolet Absorption Spectra of PAN

It was desirable to check the properties of the undegraded and degraded polynorlonitrile obtained from the Chemstrand Corporation. Samples of degraded PAN, A-78880-B, had a distinct absorption at 2950 angstroms, which remained unaltered after evacuation on the high vacuum line at room temperature and at 40°C. The evacuation was carried out to ascertain whether or not volatile products caused the increased absorption.

A 1 per cent w/v PAN, A-78880-A, in the solvent mixture was irradiated for 16 hours under vacuum. The solution was then diluted to 0.5% w/v and its absorption spectra determined. The sample was subsequently exposed to the U.V. lamp source with oxygen being bubbled into the system. The absorption spectra were then determined at various stages of the irradiation process. The results are given in Figure 22. It can be seen that the presence of oxygen not only retards the rise in absorption at 295 m μ , but also destroys the functional group causing it.



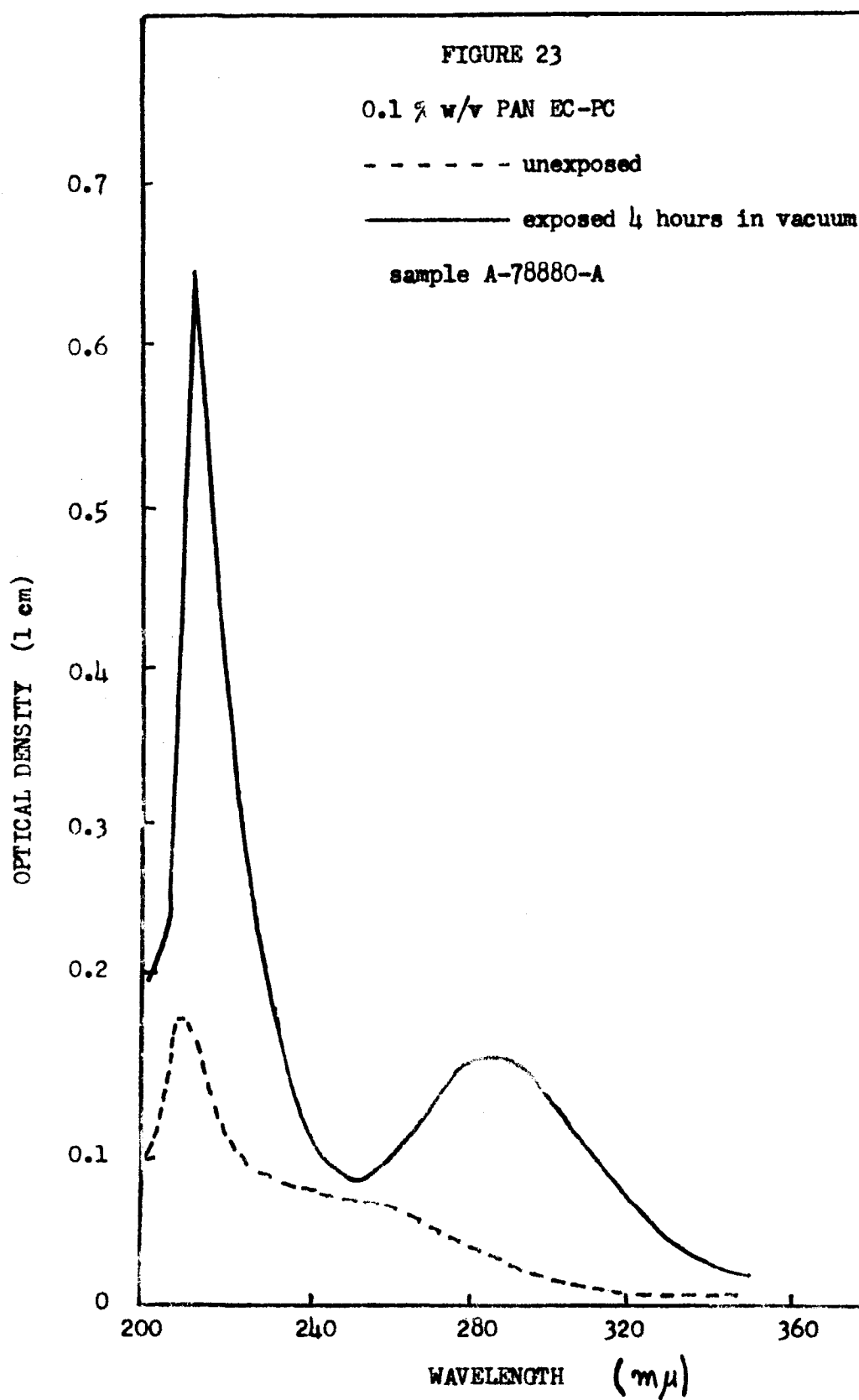
1 - original 1 % w/v PAN; 2 - 0.5 % w/v degraded in vacuum for 16 hours; 3,4,5,6 - exposed to U.V. source with O₂ bubbled into reaction vessel for 10, 20, 60, and 120 minutes respectively.

From the absorption spectrum of glutaronitrile, both degraded and undegraded, it seemed plausible that PAN should also have an absorption maximum at 216 mμ. (See Figure 23). When degraded and undegraded PAN's ultraviolet absorption spectra were determined using the Bausch-Lomb Spectronic 505, this maximum did appear. The absorption at 216 mμ. increased similarly as was the case with the polymer of lowest molecular weight when the samples were exposed to the U.V. source.

Measurement of Small Molecules

Polyacrylonitrile, A-78880-B, was exposed to the ultraviolet source for the purpose of determining whether or not small molecules such as HCN and monomer were evolved. It was degraded as a film, in solution, and in powder form.

The powder was exposed to the U.V. lamp and the gaseous material collected in a cold trap (cooled by liquid air) connected to the reaction vessel. The system was kept under continuous high vacuum by making the proper connections to the high vacuum line. The system was completely degassed before the U.V. lamp was turned on. After a four hour exposure of the polymer gaseous products crystallized in the cold trap. With the removal of the liquid air bath, they volatilized immediately. The addition of alcoholic tincture of gum guaic followed by 1:1000 CuSO_4 solution (37) to the trap indicated the



presence of small molecules. A dark blue opaque solution was formed which became lighter in colour with the evolution of gaseous products. The appearance of the blue colour is a positive test for the presence of ammonia, nitriles, and hydrogen cyanide. The gas had the distinct odour of HCN only. The polymeric material left in the reaction vessel was insoluble in DMF and light brown in colour, indicating that crosslinking had taken place.

Films were also exposed to the U.V. source, both in the presence of oxygen and under vacuum. The films approximately 23 microns (thick) were prepared by evacuating dilute solutions of PAN (2% w/v) in DMF at 40°C in glass petrie dishes. Once the film had formed it was peeled off the glass and dried in vacuum at 40°C. for 24 hours. The loss in weight of the film exposed in air was determined by observing the extent to which the weight of the polymer film extended a quartz spiral spring. The loss in weight of the film exposed in vacuum was determined by recording the weight on a gravimetric balance before and after degradation. Each sample was exposed approximately six hours. Loss of weight could not be detected in either case. However, the films turned to a yellow colour when exposed in oxygen and a dark brown when exposed in vacuum, for the period of time. The exposed films were insoluble in DMF. Upon heating, on a steam bath, the polymer dissolved

leaving coloured material in suspension.

When solutions of PAN in the solvent mixture were exposed to the U.V. light, small molecules could not be detected for concentrations of 0.1% w/v to 0.4% w/v. They were exposed in the same manner as the powder. A 1% w/v solution gave a positive test for small molecules excluding solvent molecules. The addition of copper sulphate and gum guaiac resin to any material collected in the cold trap was used as a confirmatory test.

Infrared Spectra

The infrared spectra of degraded polymer were examined in the hope of determining structural changes in the polymer. One per cent solutions in the solvent mixture were irradiated in vacuum for 40 hour periods. Samples of exposed and unexposed polymers were precipitated from the solvent mixture with distilled water. The samples were washed well with hot water and collected in fritted glass filters. After drying under vacuum for 24 hours, their spectra were determined.

Three samples of A-78880-A: one original, one reprecipitated from the solvent mixture, and one precipitated from the exposed solution were sent to the Perkin Elmer Corporation. The infrared spectrum of the original is shown in Figure 24 and that of the exposed sample in Figure 25. The doublet in the region of $1770-1780\text{ cm}^{-1}$

FIGURE 24
INFRARED SPECTRUM OF UNEXPOSED POLYACRYLONITRILE
sample A-78880-A

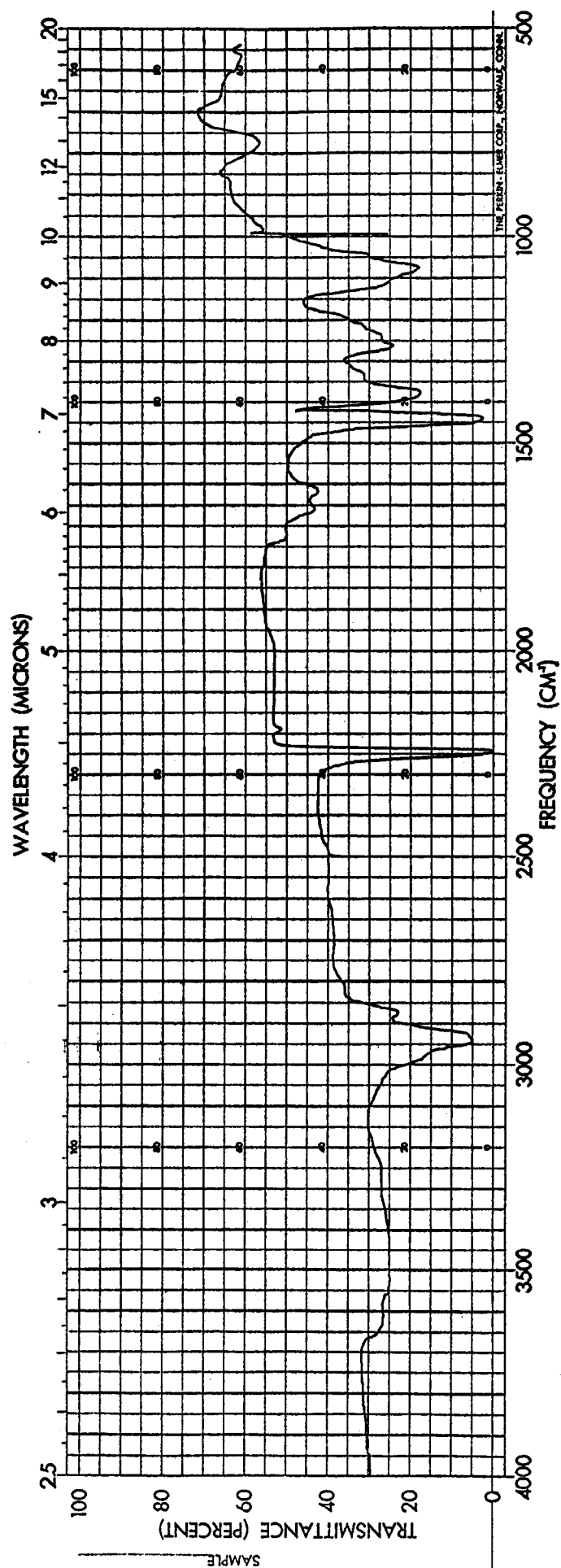
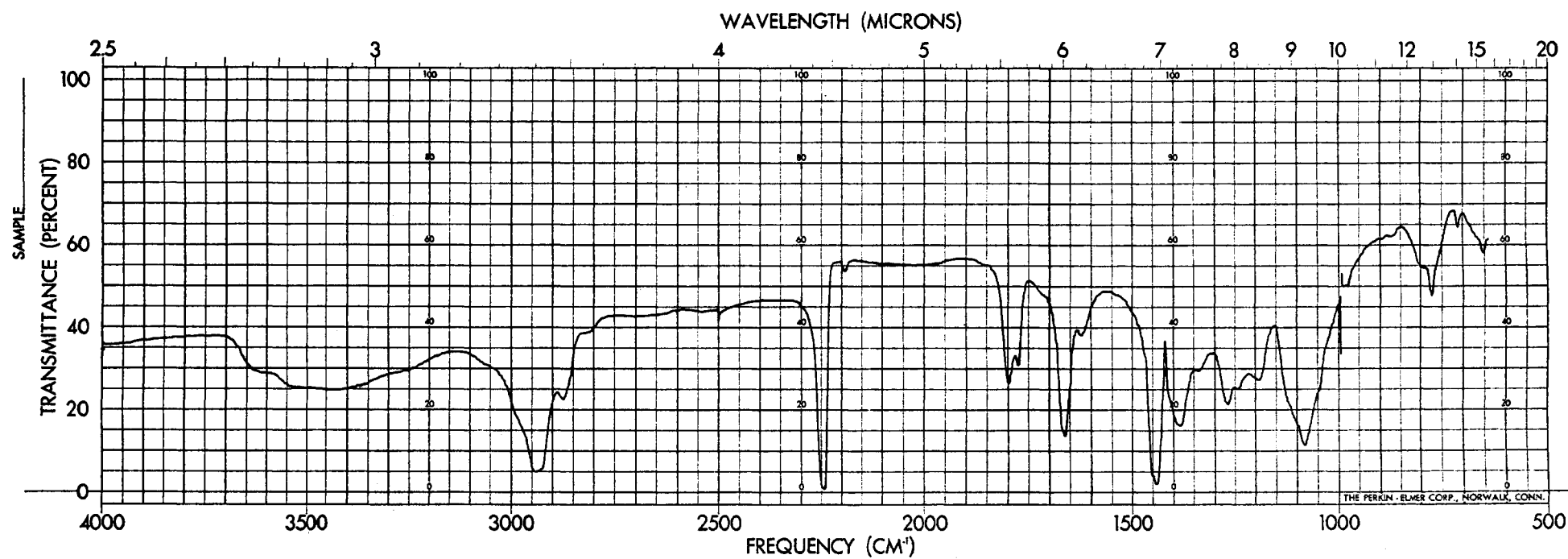


FIGURE 25

INFRARED SPECTRUM OF EXPOSED POLYACRYLONITRILE IN SOLUTION

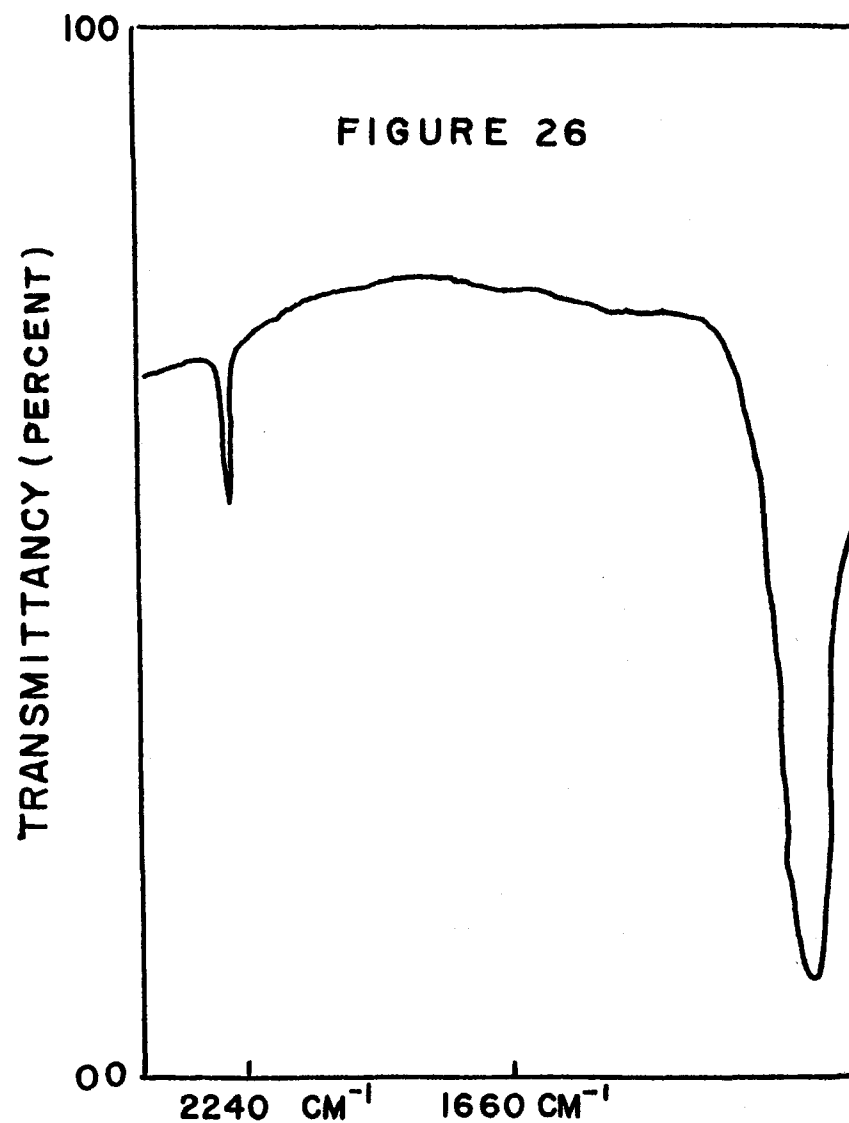
Time of Irradiation was 40 hours for sample A-78880-A



was assumed to be solvent not removed in the precipitation. A band at 1660 cm^{-1} was also reported. Perkin Elmer employed the potassium bromide pellet technique.

The infrared spectra of the same samples were also determined using our Beckman IR-5 spectrophotometer. These samples were examined in the form of Nujol mulls. The $1770\text{--}1780\text{ cm}^{-1}$ doublet, characteristic of cyclic carbonates, again appeared, but the 1660 cm^{-1} band as reported by Perkin Elmer was not present. The infrared spectrum for the same exposed polymer was also determined after it had been reprecipitated from DMF. This spectrum was identical with the unexposed sample and did not show any absorption in the $1770\text{--}1780\text{ cm}^{-1}$ region as did the sample precipitated directly from the solvent mixture (see Figure 26).

Infrared spectra were also determined for exposed and unexposed samples of glutaronitrile, and failed to show any well defined changes. Unsaturated groups were prevalent in the region of 1660 cm^{-1} , but their absorption was weak. Fifty per cent by volume solutions of glutaronitrile in chloroform were used in the Beckman IR-5 instrument.



SPECTROGRAM OF EXPOSED POLYMER
A-78880-A AFTER REPRECIPITATION
FROM DIMETHYLFORMAMIDE,(NUJOL
MULL) BECKMAN IR-5

CHAPTER VI

DISCUSSION OF KINETICS AND MECHANISM OF PHOTODEGRADATION

Kinetic Derivations

The kinetics of photodegradation has been discussed by Jellinek and Schluter (1) as a random scission process with the rate of breaking links as follows:

$$-\frac{dn}{dt} = knI_0 \quad (1)$$

where n is the number of C-C links in the main polymer chain at time t , I_0 the incident light intensity, and k a rate constant. The treatment was generalized by Jellinek (38) and the rate of breaking links was expressed as,

$$-\frac{dn}{dt} = \beta I_{abs} \quad (2)$$

where I_{abs} is the absorbed light intensity, n is the concentration of C-C links (number per unit volume), and β is the quantum yield in chain scissions per quantum absorbed.

In the particular case of the photodegradation of polyacrylonitrile, actinometry measurements gave the incident light intensity absorbed for the reaction cell of cross-sectional area A and length l in unit time. Hence when one considers the photodegradation of the polymer solution the light intensity absorbed by the cell containing

solution is
$$I_o = AI_o - AI_t \quad (3)$$

where I_o is the absorbed light intensity of the cell filled with polymer solution, I_o is the incident light intensity to the cell, I_t is the transmitted light intensity, and A is the cross-sectional area of the reaction vessel.

Now, if the Beer-Lambert law is obeyed,

$$I_t = I_o e^{-k_2 n_o l} \quad (4)$$

where k_2 is a constant, n_o is the initial concentration of links in the cell of length l .

From equation (3),

$$I_o = AI_o (1 - e^{-k_2 n_o l}) \quad (5)$$

Also, as n is expressed in C-C links per unit volume, the intensity absorbed per unit volume of polymer solution is given by,

$$I_{abs} = \frac{AI_o (1 - e^{-k_2 n_o l})}{V} \quad (6)$$

where V is the volume of polymer solution held by the reaction cell.

Equation (2) reduces to,

$$\frac{dn}{dt} = \frac{AI_o A}{V} (1 - e^{-k_2 n_o l}) \quad (7)$$

Integration yields,

$$n_o - n = \frac{AI_o A}{V} (1 - e^{-k_2 n_o l}) t \quad (8)$$

As $k_2 n_o l = 2.303E$, where $E = \log I_o/I_t$ is the optical density of the solution of thickness l , and as E is small, one obtains,

$$n_o - n = 2.303 \frac{AI_o A}{V} Et \quad (9)$$

If one introduces $S = P_0/P_t - 1$, the average number of breaks for each original chain (2), P_0 and P_t being the initial number average chain length and the number average chain length at time "t", respectively, one obtains:

$$n_0 - n = NS = 2.303 \frac{\phi I_0 A}{V} Et \quad (10)$$

where N is the concentration of polymer chains in the system,

$$\text{or } NS = N (P_0/P_t - 1) = 2.303 \frac{\phi I_0 A}{V} Et \quad (11)$$

$$\text{further } \frac{NS}{P_0} = \frac{N}{P_0} (P_0/P_t - 1) = 2.303 \frac{\phi I_0 A}{P_0 V} Et \quad (12)$$

$$\text{finally } MP_0(1/P_t - 1/P_0) = 2.303 \frac{\phi I_0 A}{V} Et \quad (13)$$

MP_0 represents the concentration of C-C links, number per unit volume " n_0 ",

$$n_0(1/P_t - 1/P_0) = 2.303 \frac{\phi I_0 A}{V} Et \quad (14)$$

Since $E = \frac{k_2 n_0 I}{2.303}$; $(1/P_t - 1/P_0)$ is independent of the

concentration of the polymer solution.

Also as $\frac{\phi I_0 A E}{V}$ and n_0 are constants during any one

experiment equation (14) reduces to,

$$1/P_t - 1/P_0 = k_3 t \quad (15)$$

where k_3 is a constant.

The degradation should also be independent of the initial chain length P_0 . If $1/P_t$ is plotted against the time of irradiation t all slopes should be equal to k_3 in equation (15).

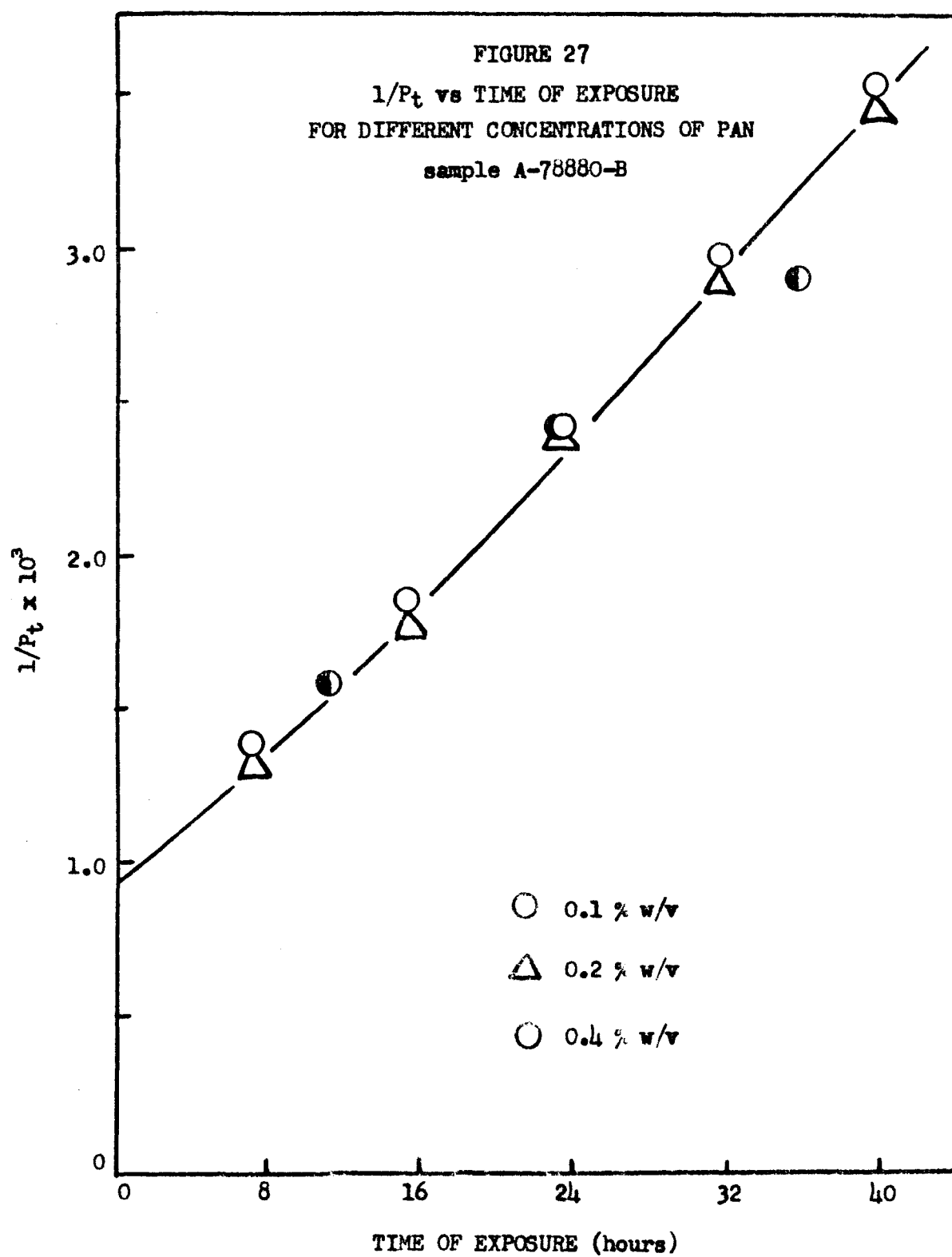
Equation (14) corresponds to equation (9) in the quoted paper (38) where $k_2 = \frac{2.303 E}{n_0 l}$

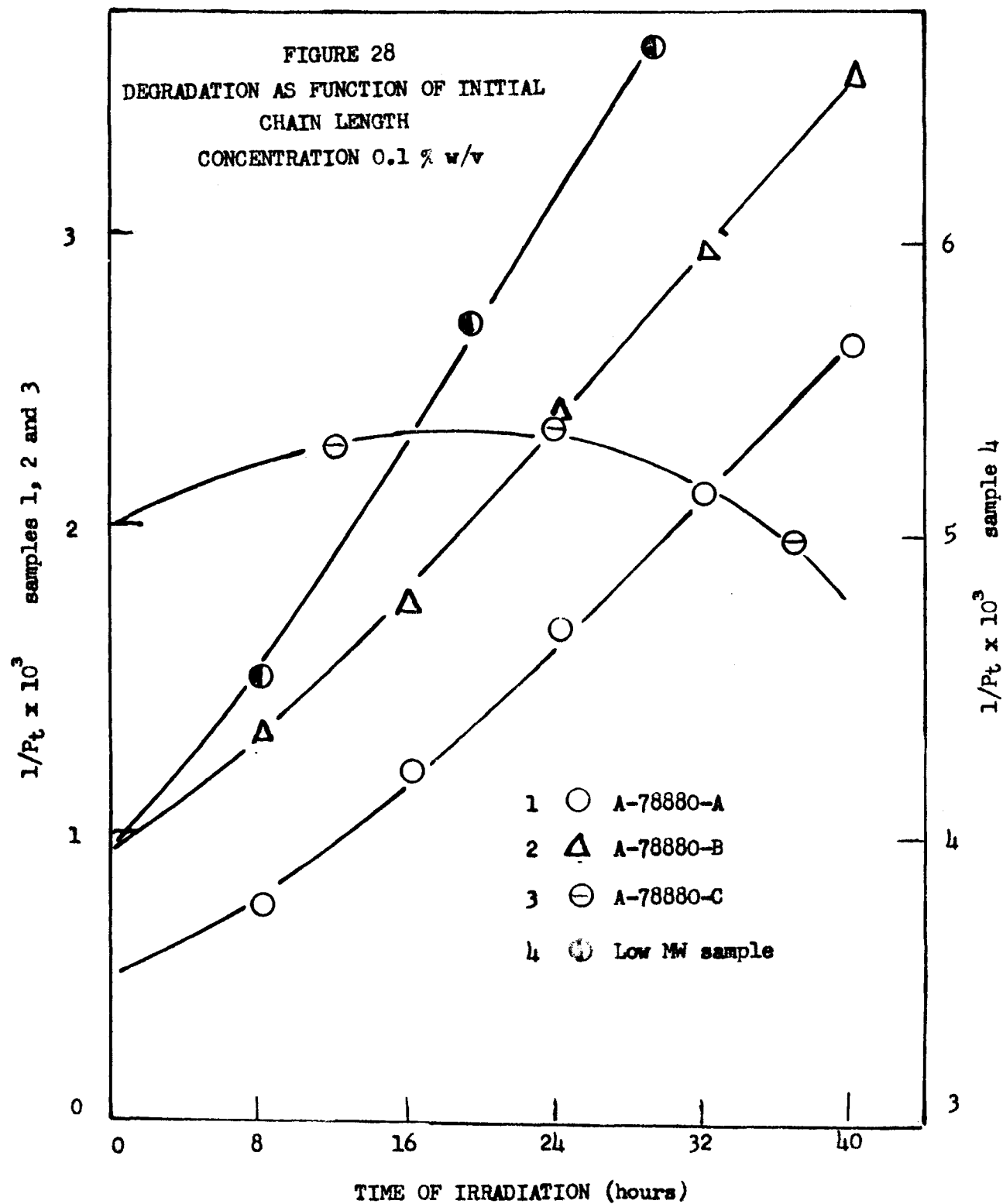
The term $\frac{I_0 A}{V}$ is retained in equation (14) as actinometer measurements gave the absorbed intensity AI_0 integrated over the cross-sectional area of the reaction vessel.

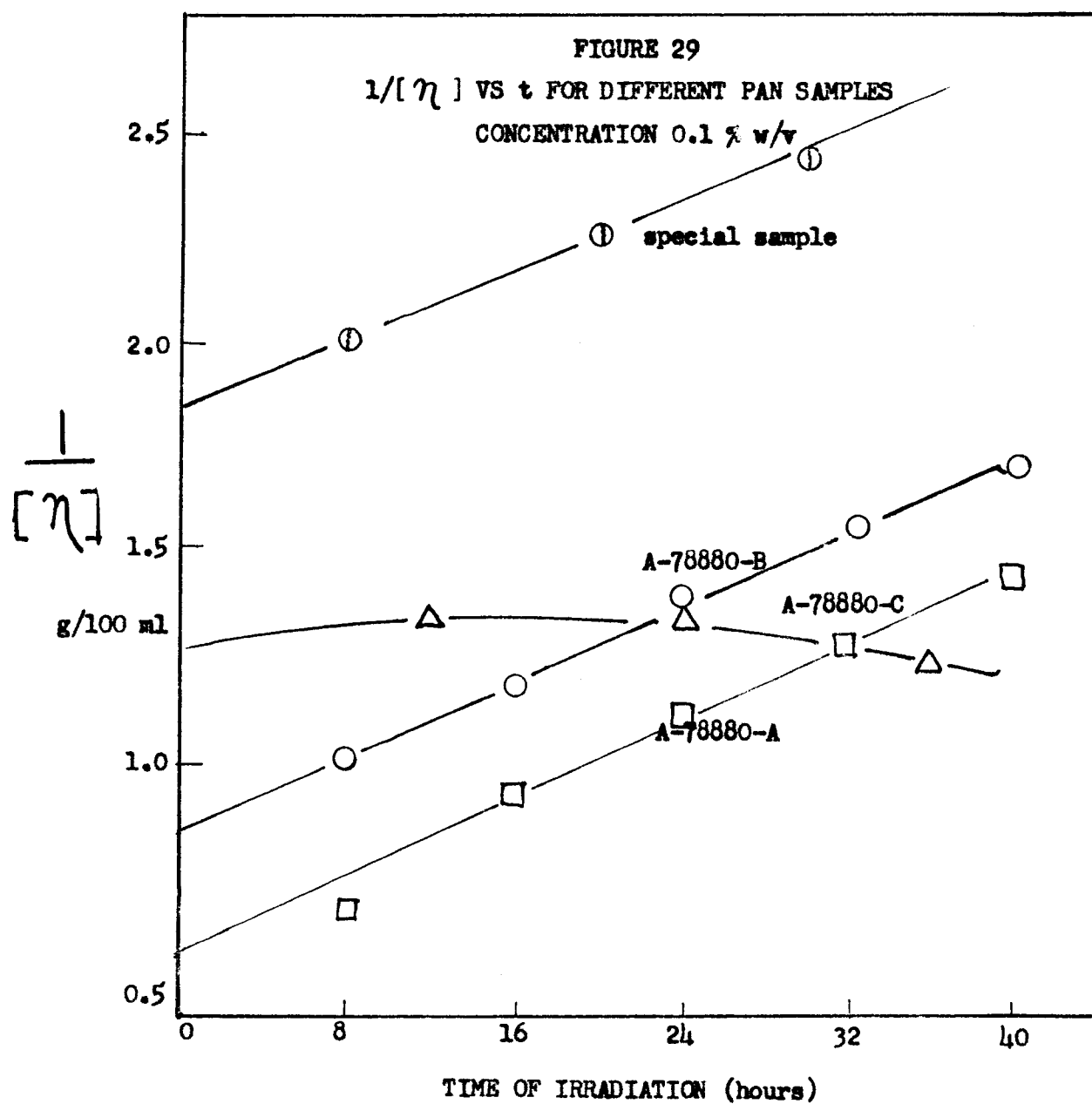
Representation of Experimental Data

By plotting all experimental results in terms of this theory, that is, $1/P_t$ versus t , straight lines should be obtained. Figure 27 illustrates the degradation process as a function of concentration for the polymer sample whose initial intrinsic viscosity in the solvent mixture was $1.21 \text{ (g/100 ml)}^{-1}$. Figure 28 illustrates the degradation of polymers of different initial chain lengths. The results of the samples prepared in this laboratory as well as the samples prepared by the Chomstrand Corporation are included. Figure 29 illustrates the degradation of the polymer sample, whose initial intrinsic viscosity was $1.21 \text{ (g/100 ml)}^{-1}$ at three different light intensities.

It can be seen that the graphical representation of the data does not follow the theory for the random scission process precisely. However, the experimental results do show that the random scission process in terms of the theory is approximately obeyed. The fact that the random scission process is not strictly obeyed may be due to the increasing absorption of the U.V. radiation







at 2537 angstroms as the degradation progressed. However, the increase in absorption is far too great to reconcile it with the small deviation of the kinetic process from the theory. It may be that the intrinsic viscosity-number average molecular weight relationship that was used may not be quite correct as there is little agreement between the relationships in Table IV. On the other hand, the basic assumption made in the theory was that the light absorption of the polymer remained constant during the degradation as only a small number of links are broken. This may not be necessarily true.

Sample A-78880-C displayed abnormal behaviour, in that it increased in viscosity during the degradation. Crosslinking could be one possible explanation for its abnormal behaviour, however, this is reserved for the discussion of the mechanisms of the degradation process.

It was also found that the experimental data could be fitted to an empirical relationship (see Figure 29) where $1/[\eta]$ plotted against "t", time of irradiation, gave straight lines.

The rate constants of degradation for different initial chain lengths are summarized in Table XV.

TABLE XV

RATE CONSTANTS FOR DIFFERENT SAMPLES
FOR 0.1 W/V SOLUTIONS AND CONSTANT I_0

<u>Sample</u>	<u>Rate Constant (hr^{-1})</u>
A-78880-A	6.05×10^{-5}
A-78880-B	6.57×10^{-5}
A-78880-C	abnormal sample
low m.w. sample	9.60×10^{-5}

The fact that the low molecular weight sample absorbed appreciably at 2537 \AA^0 may account for its high rate constant. Samples A-78880-A and A-78880-B, which were prepared in a similar manner have values for the rate constants which are fairly close.

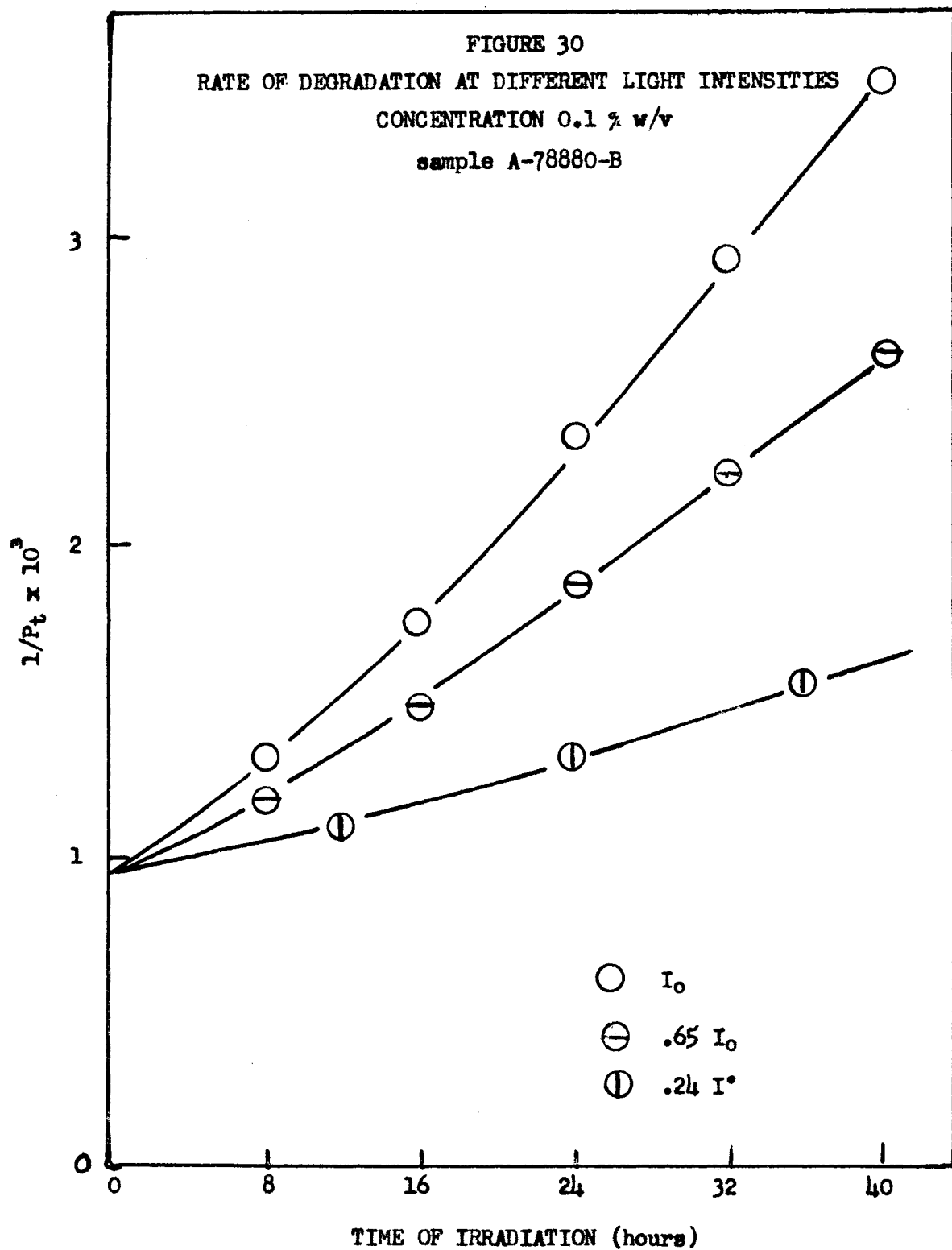
Rate of Degradation as a Function of Incident Light Intensity

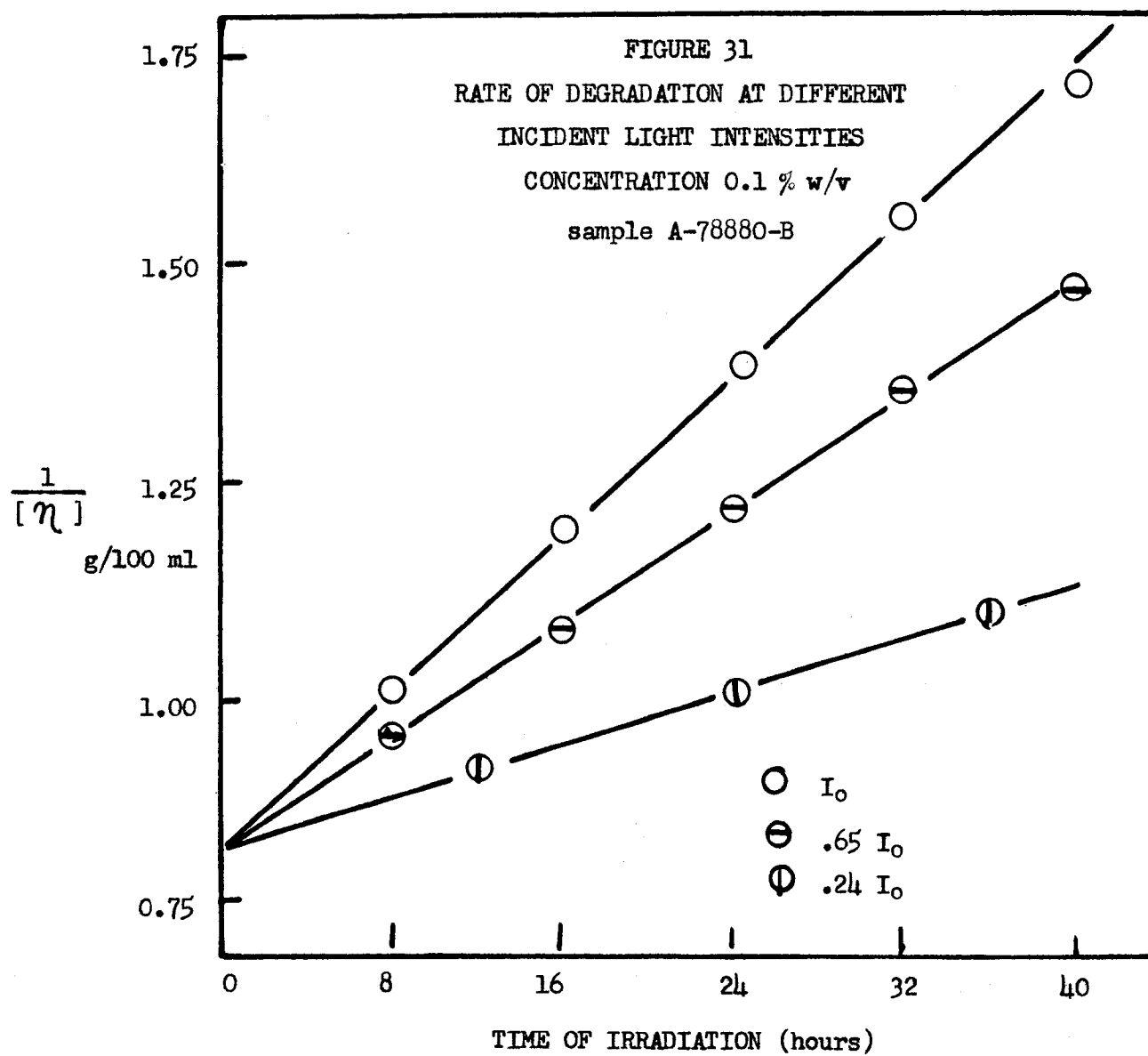
The rate of degradation for different light intensities has been represented in a variety of ways. First, the theory for random scission was assumed to hold. In other words, the slopes of the lines in Figure 30 were determined on the basis of the equation,

$$1/P_t - 1/P_0 = kt$$

where k is the slope and $1/P_0$ the intercept. Second, the empirical relationship, where $1/$ plotted against exposure time represented a straight line, was used. This relationship is illustrated in Figure 31. In actual fact, the equation of the lines is,

$$1/[\eta]_t - 1/[\eta]_0 = kt$$



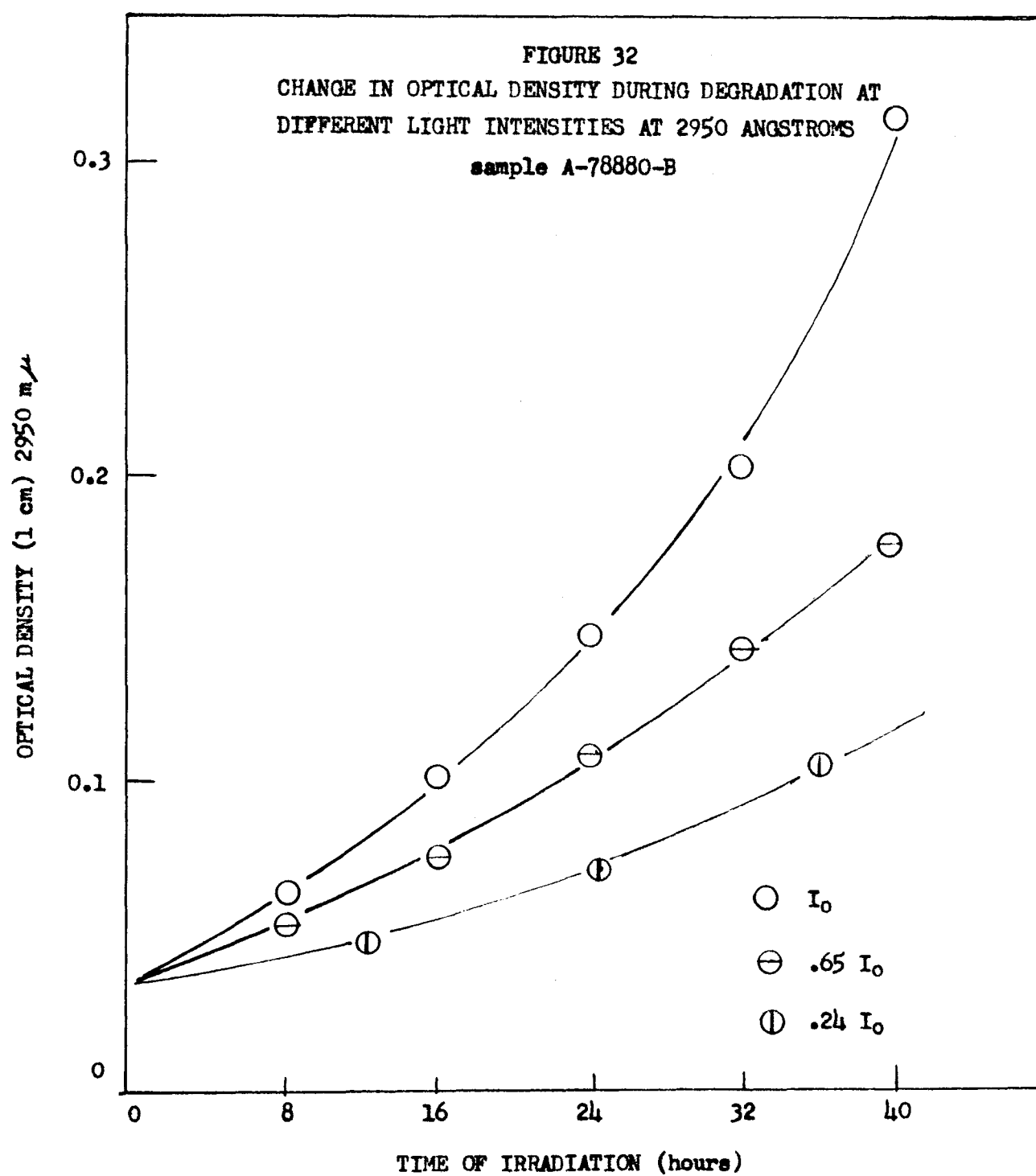


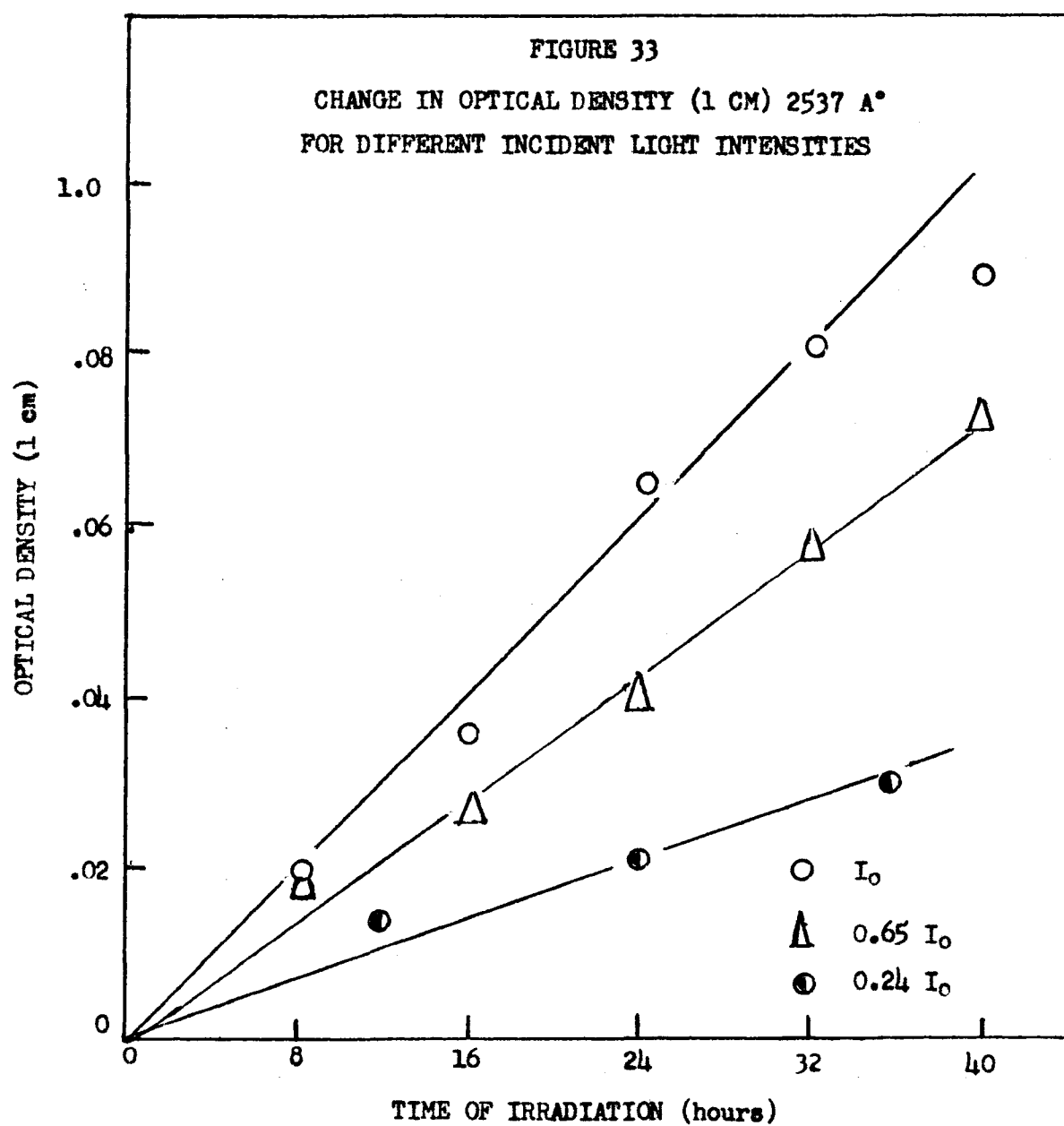
The slopes for each line were determined and compared with those determined above on a relative basis. Two other relationships were plotted to ascertain whether or not it indicated that the increase in absorption of the polymer sample is a function of the light intensity. The increase in absorption at 2537 angstroms as a function of the incident light intensity could be determined quite readily as the increase was linear with the different intensities. This, however, was not the case for the increase in absorption of the polymer at 2950 angstroms. The increase in optical density of the polymer solutions at 2537 and 2950 angstroms is illustrated in Figure 32 and Figure 33, respectively. The results are summarized in Table XVI.

TABLE XVI

DEGRADATION AS A FUNCTION OF INCIDENT LIGHT INTENSITY

Relative Light Intensities	$\frac{1}{[\eta]_t}$ vs t (Slope ₁ vs t (g/ml·hr ⁻¹))	$1/P_t$ vs t (Slope ₂ vs t (hr ⁻¹))
I_0	2.25×10^{-2}	6.57×10^{-5}
$0.65 I_0$	1.64×10^{-2}	3.92×10^{-5}
$0.24 I_0$	0.72×10^{-2}	1.52×10^{-5}
Relative Light Intensities	Relative Slope ₁	Relative Slope ₂
I_0	1	1
$0.65 I_0$	0.73	0.60
$0.24 I_0$	0.32	0.23





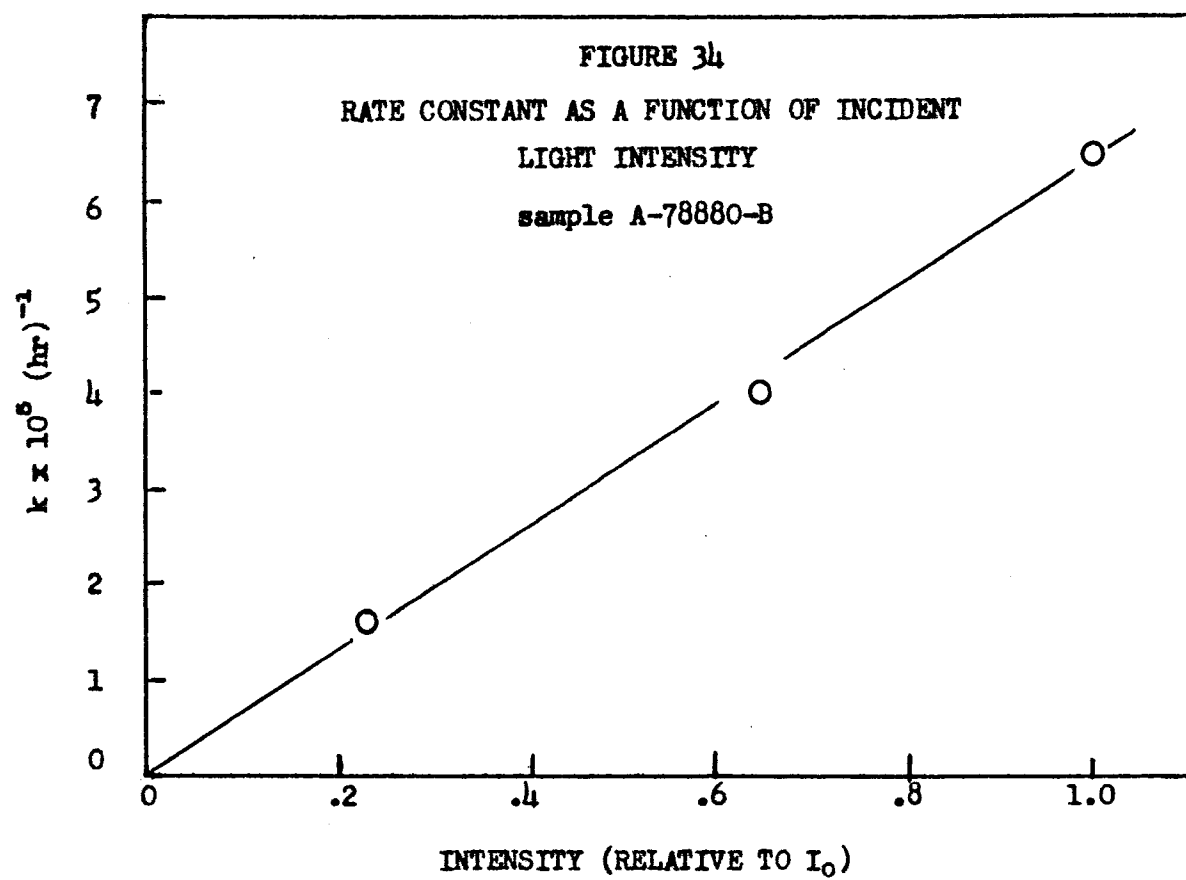
The optical density at 2537 \AA after 8 hours also appears to increase linearly with relative slopes paralleling the relative intensities.

<u>Slope of Increasing Optical Density (see Fig. 33)</u>	<u>Relative Slopes</u>	<u>Relative Light Intensities</u>
2.85×10^{-3}	1	I_0
1.82×10^{-3}	0.64	$0.65 I_0$
0.77×10^{-3}	0.27	$0.24 I_0$

As the relative slopes of the plot of $1/P_t$ versus t parallel the relative intensities, it becomes evident that the theory of random chain scission is approximately obeyed.

Determination of Quantum Yield

If one considers the theory of random scission to be applicable to the experimental results, one may conclude that the quantum yield is constant for different incident intensities. In other words the rate constants plotted as a function of the intensity should give a straight line (see Figure 34). The question then arises as to what the optical density is for the polymer solution for the chain scission process only. As the absorption of the solution increased during the degradation, an average value was taken for the optical density of the solution in the reaction vessel. Considering the degradation of a 0.1% w/v solution of PAN at an incident light intensity of 2.58×10^{17}



quanta per second incident to the cross-sectional area of the reaction vessel, the quantum yield may be calculated as follows:

The optical density at 2537 Å⁰ for the exposed samples was 0.090 for a one cm. cell after 40 hours of exposure. As the reaction vessel was 3 cm. in length the optical density is .270 for the reaction vessel. Also as the optical density for the polymer solution appears to be zero by extrapolation of the optical density to zero time (see Figure 33) an average value of $0.270/2 = 0.135$ was taken for the quantum yield calculation.

From equation (14),

$$\phi = \frac{n_0 V (1/P_t - 1/P_0)}{2.303 I_0 A \epsilon t}$$

where $\epsilon = .135$

$$n_0 = \frac{.001}{53} \times 6.023 \text{ links per cm}^3$$

$$V = 33.00 \text{ ml.}$$

$$1/P_t - 1/P_0 = 2.53 \times 10^{-3}$$

$$AI_0 = 2.58 \times 10^{17} \text{ quanta/sec.}$$

$$\text{subst. } \phi = \frac{2.53 \times 10^{-3} \left(\frac{.001}{53} \right) 33 \times 6.023 \times 10^{23}}{2.303 \times 2.58 \times 10^{17} \times 0.135 \times 40 \times 3600}$$

$$\text{or } \phi = 0.84 \times 10^{-4} \frac{\text{chain scissions}}{\text{quanta absorbed}}$$

On the other hand if one determines the quantum yield between the eight and forty hour exposure periods a lower value is obtained.

The average optical density is taken as,

$$OD_{AVE} = \frac{E_{40} - E_8}{2} = 0.165$$

which then yields,

$$\phi = \frac{2.17 \times 10^{-3} \left(\frac{1001}{53} \right) 33 \times 6.023 \times 10^{23}}{2.58 \times 10^{17} \times 2.303 \times 0.165 \times 32 \times 3600}$$

$$\phi = 0.72 \times 10^{-4} \frac{\text{chain scissions}}{\text{quanta absorbed}}$$

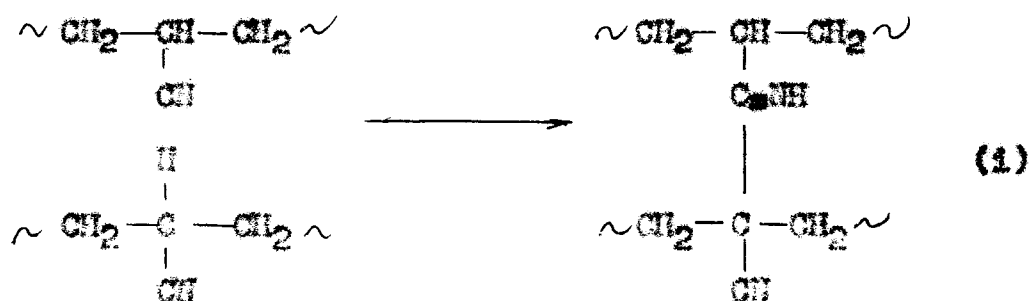
The above values for the quantum yield are only average values based on the change in optical density at 2537 angstroms. However, the values are in good agreement with those obtained for other polymers (see Table VIII).

Mechanisms of Photodegradation of PAN

It has become increasingly evident that the degradation of polyacrylonitrile in solution is not a simple problem. One can assume from the experimental results that the degradation by photochemical means does follow a random scission process, however, the results indicate that other photochemical processes take place also in the system.

The polymer prior to degradation has absorption properties which are characteristic of dinitriles such as glutaronitrile. The large absorption of the polymer prepared in this laboratory at 265 mμ. may support Schurz's (10, 11) theory that the 265 mμ. absorption may

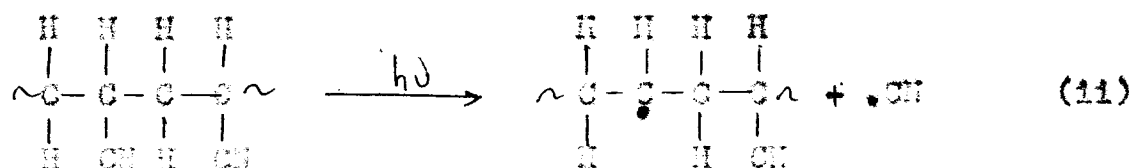
in part be due to iminisation



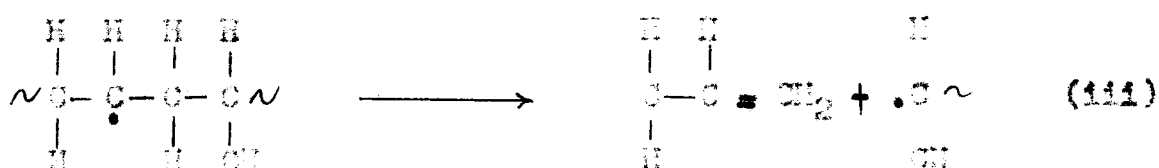
The above reaction may also have occurred in the photodegradation of sample A-78880-C where the absorption of the polymer increased in the region 260-280 mμ. The fact that the absorption at 265 mμ. disappears in the sample prepared in this laboratory, as well as the Chemstrand samples would therefore indicate that the imine groups, $\text{C}=\text{NH}$, appear to be weak links in the polymer structure and are subject to scission. These scissions are independent of the main kinetic scheme and should not be confused with the random chain scission process. If this were the actual case, then the increased absorption for the photodegraded sample A-78880-C might be due to some other mechanism.

Jellinek and Schnitzer (1) have postulated several mechanisms which might occur during the photodegradation of polyacrylonitrile in solution.

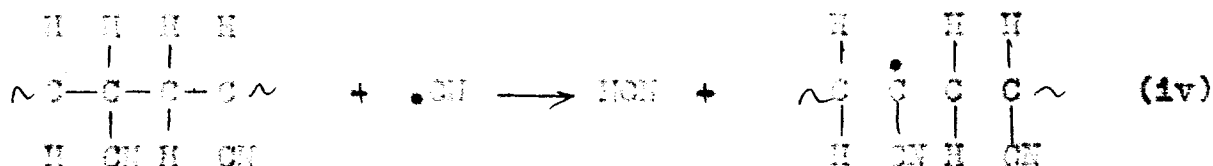
"Some tentative suggestions as to the possible reactions leading to chain scission" are given on page 104.



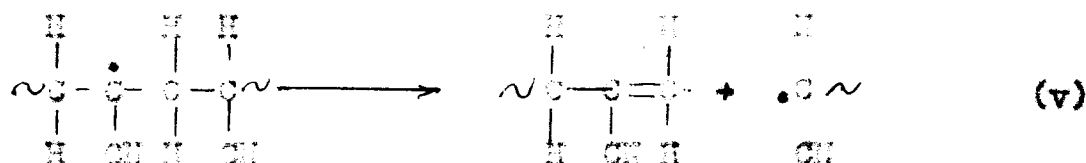
"This reaction can lead to chain scission,"



It was proposed that the " $\cdot\text{CN}$ radical could react with α hydrogen atoms leading to further chain scission".

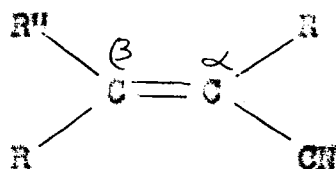


Although the course of the degradation is speculative the above mechanisms are plausible. On the other hand, if one considers the degradation in terms of the new absorption characteristics of the photodegraded polyacrylonitrile, reaction (iv) may be followed by,

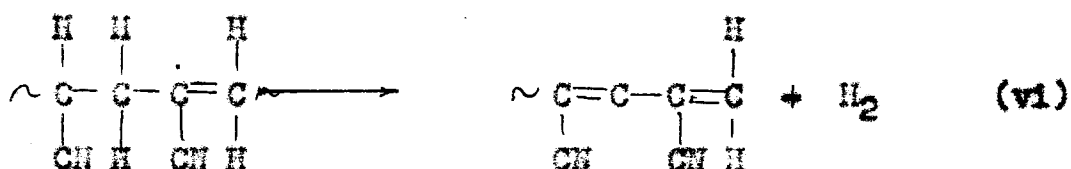


A dead polymer chain would occur with a terminal olefin. If one considers the rise in absorption at 216 mμ., this reaction may be a plausible one. Heilmann et al (39)

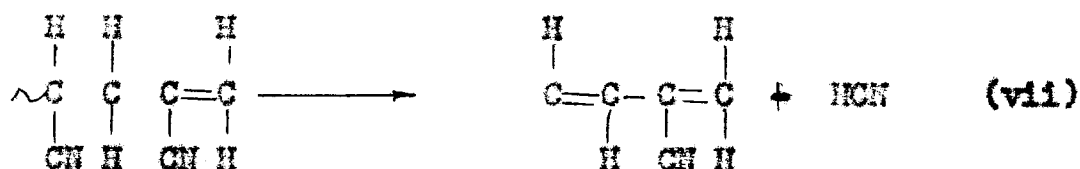
have studied the absorption characteristics of ethylenic nitriles of the type,



which exhibit strong absorption in the region 208-216 μ , depending on the nature of the substituents alpha and beta to the nitrile. The 216 μ , absorption increase could certainly be due to olefinic nitrile in the photodegraded polymer,



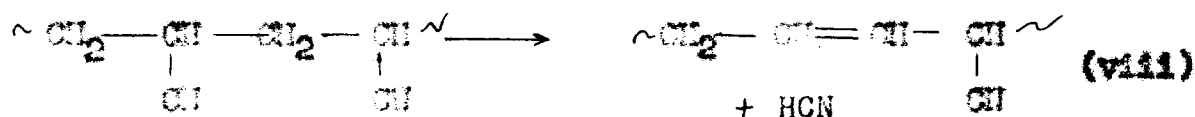
OR



As the α hydrogens are vulnerable it is not unreasonable that hydrogen may be removed in the reaction. Durlant and Taylor (6) measured the release of small amounts of hydrogen in their radiation experiments on films of polyacrylonitrile.

If one postulated that this mechanism were the correct one, then the absorption at 295 μ , might be due to the presence of conjugated systems in the photodegraded

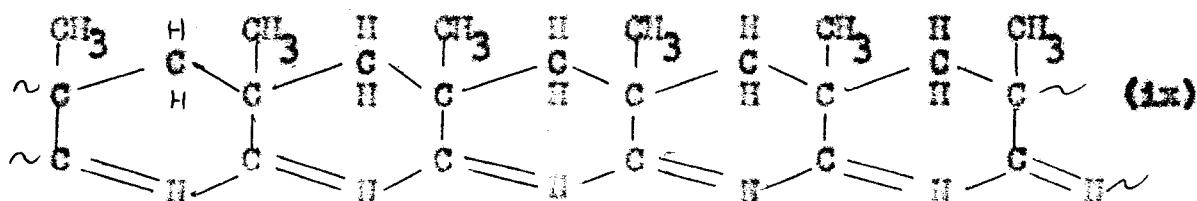
polymer. Reaction (vi) was postulated on the basis of the experimental evidence, that is, no hydrogen cyanide could be detected in the photodegraded solutions with a concentration of 0.1% w/v PAN. Straus and Madorsky's (3) postulate that hydrogen cyanide is removed by thermal degradation in the following manner,



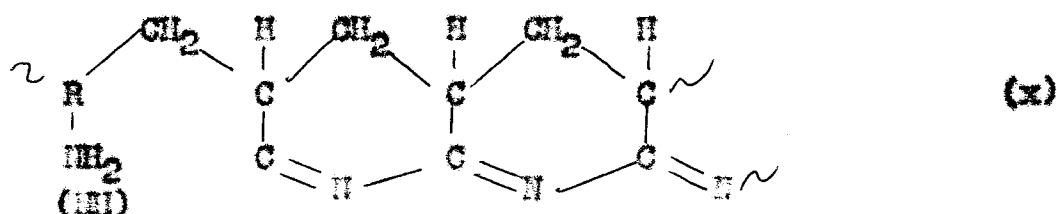
does not substantiate any of the physicochemical evidence obtained in this laboratory unless hydrogen cyanide is removed to give a conjugated system which may give rise to absorption at 295 mμ. Straus and Madorsky's (3) postulation that chain scission occurs followed by an unsnipping of monomer may also substantiate the increase in absorption at 216 mμ, which is in the region of monomer absorption (see Chapter II).

Internal cyclization is also another possibility in the photodegradation of the polyacrylonitrile. Although there has been little evidence put forward for the actual existence of such groups, several authors have offered the cyclic naphthyridine type structure as a result of thermal pyrolysis. Grassie and Mellville (12) in their thermal degradation of polymethacrylonitrile, concluded that the following ring structure was a result of the

pyrolysis,

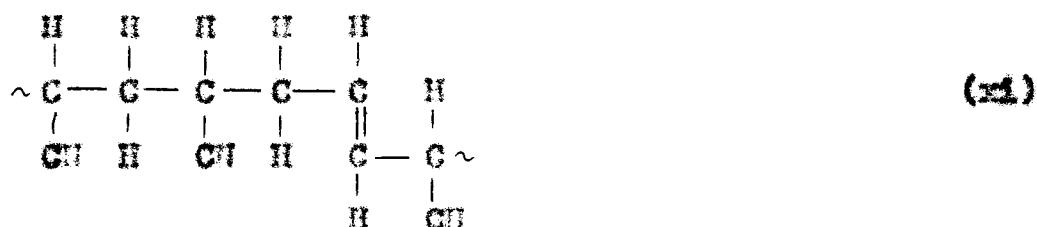


Burlant and Parsons (5) speculated from their pyrolysis experiments on PAN that cyclization proceeded in a similar manner to give,

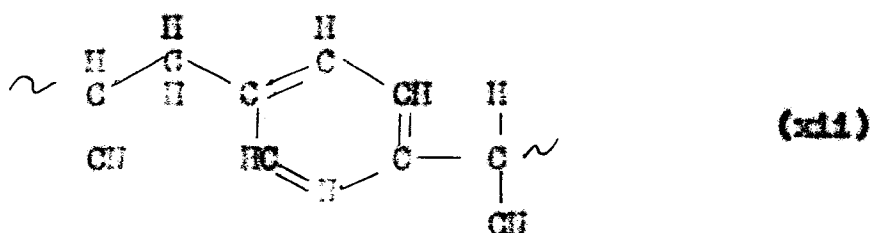


Burlant and Parsons made an intensive study of infrared spectra of the thermally degraded polymer and concluded that this cyclic structure was quite probable. They also reported that ammonia formed during the pyrolysis. Straus and Madorsky (3) did not find any ammonia in their volatile fractions of the thermally degraded polymer.

On the other hand Kobayashi (6) infers that cyclization occurs first by removal of hydrogen cyanide in the polymer to give,



which cyclises to give,



As substituted pyridines absorb in the region of 300 mμ, the cyclic structures could occur in the photodegraded polymer. However, as there is a large number of compounds that absorb in the same regions as the photodegraded polymer, one can only speculate as to what change in structure has taken place in the polymer.

Although discussion of the abnormal sample has been reserved, little can be said to substantiate the increase in the viscosity of the photodegraded material or its absorption at 285 mμ. It is possible that impurities or small molecules in the polymer existed that caused the abnormal behaviour.

CHAPTER VII

SUMMARY AND CONCLUSIONS

The photodegradation of polyacrylonitrile in solution may be summarized under the following headings:

(i) Recalculation of Previous Results -

Jellinek and Schlöter's (1) results were recalculated using the Cleland-Stockmayer equation (17). The recalculated results give a "rate constant-incident light intensity" relationship which is consistent with the generalized theory of random chain scission (38) for photodegradation of polymers in solution (see Figure 4).

(ii) Photodegradation as a Function of Concentration - The

photodegradation of polyacrylonitrile is independent of concentration in the solvent mixture. The yellowing of the solutions whose concentrations were 0.4% w/v PAN did not affect the degradation process markedly. Only after prolonged exposure did the results deviate. This was attributed to the high absorption of the solutions which caused a high degree of fluorescence in the front part of the reaction cell.

(iii) Photodegradation as a Function of Chain Length -

Degradation of polymer samples of different initial intrinsic viscosities followed the same pattern; that is, the degradation appeared to be independent of the initial intrinsic viscosity. Conversion of the data to the chain lengths and plots of $1/P_t$ vs. t gave different slopes. It was assumed

that other photochemical processes were operative in the system, which caused the deviations or the intrinsic viscosity-number average molecular weight relationship is not correct.

(iv) Photodegradation as a Function of the Incident Light Intensity - The degradation bears a direct relationship to the first power of the absorbed light intensity. These results complement the recalculated results of Jellinek and Schindler (1). The quantum yield for the photochemical degradation of polyacrylonitrile is reported as 0.8×10^{-4} chain scissions per quanta absorbed.

(v) Absorption Spectra - The photodegradation resulted in the disappearance of the 265 mμ. absorption and an increase in absorption of 216 mμ. and 295 mμ. The increase in absorption was the same in samples A-78880-A, A-78880-B, and the sample prepared in this laboratory indicating that the same photochemical processes were operative in the different samples. Sample A-78880-C exhibited abnormal behaviour for which no plausible explanation could be offered, without exact knowledge of the history of the sample.

Mechanisms for the chain scission process were also postulated which could support the appearance of the new ultraviolet absorption characteristics of the photodegraded polymer solutions. Infrared spectra did not indicate any structural changes in the polymer.

(vi) Photolysis of a Model Compound -

Glutaronitrile was exposed to the U.V. source in different solvents. Similar absorption spectra were observed for the exposed polymer and glutaronitrile in the ethylene carbonate-propylene carbonate solvent mixture. The photolysis of glutaronitrile in ethanol and methanol gave different absorption spectra. A survey of the literature did not give any information on possible products of the photolysis.

(vii) Measurement of Small Molecules - The

photodegradation of polyacrylonitrile in bulk in vacuum, resulted in the evolution of hydrogen cyanide. In the photodegraded solutions of 0.1%, 0.2%, and 0.4% w/v PAN, all tests for hydrogen cyanide, nitriles, and ammonia were negative. Only at concentrations of polymer greater than one per cent were the tests for small molecules positive.

Films were also exposed to the U.V. radiation. Crosslinking occurred both in vacuum and in the presence of oxygen with no apparent loss of weight for the films.

(viii) Oxidative Degradation - Photodegraded

polymer solutions were also exposed to the U.V. radiation in the presence of O_2 . The exposure resulted in the decrease of the 295 mμ. absorption of the polymer solution.

The results of the photodegradation of polyacrylonitrile in solution indicate that chain scission reactions of other polymers by ultraviolet radiation also

can be studied in solution, and a study of the ultraviolet absorption spectra would give tentative suggestions as to mechanisms of chain scission and other photochemical reactions.

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